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CORRECTION

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p. 325. In equations [1], [2], and [3], n should read n^2.

p. 326. In the line above equation [9], U should read $U_+^{(1)}$.

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THE PREPARATION OF D-*ARABO*PENTURONIC ACID AND D-*THREO*- AND D-*ERYTHRO*-TETRURONIC ACIDS[1]

BY P. A. J. GORIN[2] AND A. S. PERLIN

ABSTRACT

D-Glucurono-γ-lactone, D-galacturonic acid, and potassium D-glucuronate have been degraded in good yield to D-*arabo*penturonic, D-*threo*tetruronic, and D-*erythro*tetruronic acids, respectively, using lead tetraacetate in acetic acid solvent as the reagent.

INTRODUCTION

Earlier papers (11, 12) have described lead tetraacetate as a reagent useful for the stepwise degradation of sugars. It has been shown, for example, that D-glucose and L-sorbose may be degraded respectively to D-erythrose and L-glyceraldehyde in excellent yield. In the present paper it is shown that a similar reaction can be utilized as a convenient method for preparing D-*arabo*-penturonic acid and D-*erythro*- and D-*threo*-tetruronic acids from the related higher-order member of the series. D-*Arabo*penturonic acid and its barium salt have been prepared by Machida (8) from 2,3-*O*-isopropylidene-D-mannono-γ-lactone by lead tetraacetate oxidation followed by acid hydrolysis. D-*Erythro*-tetruronic acid (3) and L-*threo*tetruronic acid (4) have been shown to be present in the ozonolysis products of the enol of 5-keto-4-deoxy-D-mannosaccharo-3,6-γ-lactone and the corresponding D-gluco-derivative, respectively. The 2,3-di-*O*-acetyl methyl ester of the latter uronic acid has also been reported (7).

Trial experiments showed that D-glucurone in acetic acid containing a little water (1) rapidly consumed one mole of lead tetraacetate oxidant. Under similar conditions D-galacturonic acid took up 2.2 moles and potassium D-glucuronate 1.9 moles of oxidant; thereafter the uptakes of the oxidizing agent were relatively slow. These amounts of lead tetraacetate consumed during the initial rapid stage of the reaction were consistent with virtually stoichiometric conversion of the compounds to penturonic and tetruronic acids. Accordingly, the oxidations were repeated on a preparative scale.

The product from D-glucurone (I), after oxidation with one mole of lead tetraacetate followed by hydrolysis of the formate ester group, was shown

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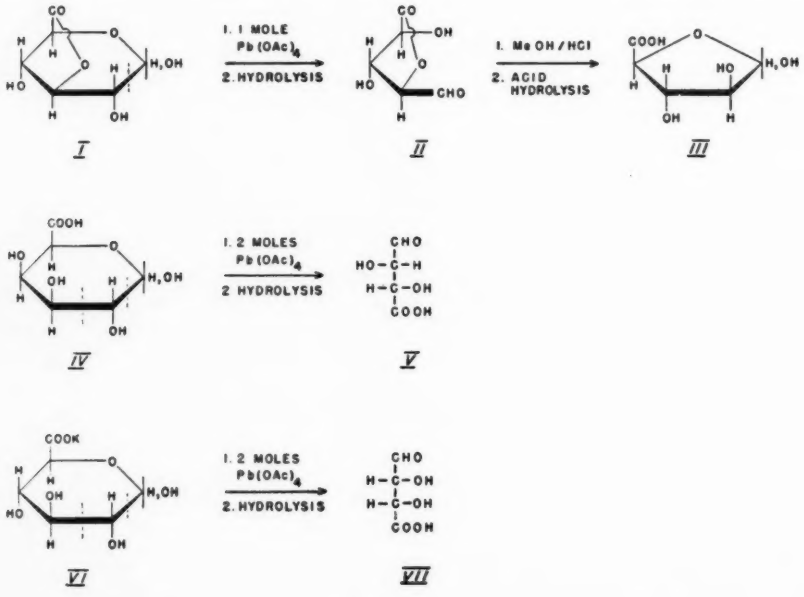
[2]*National Research Council of Canada Postdoctorate Fellow, 1955–56.*

to contain both D-*arabo*penturono-lactone (II) and D-*arabo*penturonic acid (III). This mixture was characterized as follows: reaction of the mixture with diazomethane in ethereal methanol gave a sirupy mixture of methoxyl content 6.9%, corresponding to 0.35 equivalents of free acid and 0.65 equivalents of lactone in the original oxidation product. Also, reduction of the lactone–acid mixture gave mainly crystalline D-arabitol (13) and a trace of D-lyxono-γ-lactone (detected on a paper chromatogram). Treatment of the oxidation product with acetone containing a little sulphuric acid followed by methylation with diazomethane in methanol–ether gave, in small yield, a crystalline material which was identified as 1,2-*O*-isopropylidene-D-*arabo*-penturonic acid methyl ester. The above mixture with hot methanolic hydrogen chloride gave methyl-D-*arabo*pentofurononoside methyl ester which was purified by distillation. Sirupy D-*arabo*penturonic acid could be obtained from this substance by hydrolysis with hot aqueous formic acid and was characterized by conversion with aqueous sodium borohydride to crystalline D-lyxono-γ-lactone (2). The structure of the methyl ester furononoside was confirmed by reduction with aqueous sodium borohydride to methyl-αβ-D-arabofuranoside which was hydrolyzed in hot aqueous formic acid to D-arabinose, characterized as its crystalline toluene-*p*-sulphonylhydrazone (6).

D-Galacturonic acid (IV) was oxidized with two moles of lead tetraacetate. The product appeared to be a monoformate ester from its characteristic infrared spectrum, with strong peaks at 1725^{-1} and 1170^{-1} cm. (15), and from alkaline saponification data. Since hydrolysis of the formate ester derivative occurred on standing, it is possible that the oxidation product originally



contained more than one formate group and partly hydrolyzed before the reaction mixture could be worked up. A separate oxidation under similar conditions, followed by hydrolysis of the formate esters, furnished in very good yield D-*threo*tetruronic acid (V) which gave a single spot on a paper chromatogram with the *p*-anisidine hydrochloride spray (5). Its R_F value was less than D-*arabo*penturonic acid, thus suggesting that the tetruronic acid exists in solution as the dimer. The uronic acid was characterized as its crystalline 2,4-dinitrophenylhydrazone and by conversion on sodium borohydride reduction to D-threonolactone which gave crystalline D-threonic acid phenylhydrazide after treatment with ethanolic phenylhydrazine (9). Methanolic hydrogen chloride reacted with D-*threo*tetruronic acid to give the methyl ester dimethyl acetal, which was purified by distillation.

Oxidation of potassium D-glucuronate (VI) in acetic acid with two moles of lead tetraacetate afforded, in about 50% yield, a product which contained mainly D-*erythro*tetruronic acid (VII). On a paper chromatogram the tetruronic acid moved at practically the same speed as D-*threo*tetruronic acid and thus also appears to be dimeric in solution. A small proportion of a faster moving compound, probably due to overoxidation, was shown to be present. The uronic acid was characterized by reduction with aqueous sodium borohydride, to give crystalline L-erythrono-γ-lactone (14). Also, cold methanolic hydrogen chloride converted the tetruronic acid to the methyl ester dimethyl acetal which could be purified by distillation.

EXPERIMENTAL

Paper chromatography was carried out on Whatman No. 1 filter paper using *n*-butanol–ethanol–water (40:11:19 v/v) and ethyl acetate – acetic acid – formic acid – water (18:3:1:4 v/v) as solvents. The terms R_{gal}, R_{rh} are used to denote distances travelled on the paper chromatogram by a compound relative to galactose and rhamnose, respectively. Evaporations were carried out under reduced pressure at 40°C. Optical rotations were measured at 27°C.

Oxidation of D-*Glucurono-γ-lactone with Lead Tetraacetate*

D-Glucurone (25 mgm.) was dissolved in water (0.2 cc.) and added to acetic acid (25 cc.). The solution was treated with a 1% solution of lead tetraacetate in acetic acid (25 cc.). At intervals aliquots (3 cc.) of the mixture were removed and added to an aqueous solution (10 cc.) containing potassium iodide (0.7 gm.) and sodium acetate (4 gm.). The iodine liberated was titrated with 0.1 *N* sodium thiosulphate. A blank determination was also carried out. The following results were obtained:

Oxidation time (min.)	2	5	10	30	60	131
Molar uptake of lead tetraacetate	0.99	1.01	1.04	1.08	1.18	1.40

On a preparative scale finely powdered D-glucurone (3.56 gm.) was stirred vigorously in a solution of lead tetraacetate (12.6 gm.; 1.4 equivalents) in acetic acid (350 cc.). After six minutes the suspension had dissolved and 10%

oxalic acid in acetic acid (30 cc.) was added to decompose excess oxidant. After it was stirred for 30 min. the solution was filtered and the filtrate evaporated to a sirup which was dissolved in water (50 cc.). After 18 hr. the solution was treated with Amberlite IR-120 and evaporated to a sirup (3.23 gm.). The product, detected by the *p*-anisidine hydrochloride spray (5) after running on a paper chromatogram in the acidic solvent, gave much streaking, perhaps because of the ready conversion of the lactonic material to the free D-*arabo*-penturonic acid. The sirup had, on successive days, $[\alpha]_D$ +57°, +55°, +52°, +51°, and +49° (*c*, 3.43, water).

To determine the proportion of lactone to free acid in the mixture the sirup (293 mgm.) was dissolved in methanol (30 cc.) and ethereal diazomethane added until the yellow color persisted. The solution was evaporated to a sirup which was dissolved in acetone. A little insoluble material was filtered off and the filtrate was evaporated to a sirup (282 mgm.) which had –OMe 6.9%. This value corresponds to 0.35 equivalents of free acid and 0.65 equivalents of lactone in the starting material. When the sirup was run on a paper chromatogram using the neutral solvent two spots with R_{rh} 1.26 and R_{rh} 1.48 of roughly equal intensity were detected by spraying with ammoniacal silver nitrate (10).

D-*Arabitol*

The lead tetraacetate oxidation product from D-glucurone (264 mgm.) in water (10 cc.) was treated dropwise with a solution of sodium borohydride (150 mgm.) in water (10 cc.). After 18 hr. excess reductant was destroyed with acetic acid, the solution was passed through a column of Amberlite IR-120 and evaporated to dryness. The residue was dissolved in methanol and the solution evaporated to a sirup, the process being repeated six times in order to remove boric acid as volatile methyl borate. The product (245 mgm.) gave, on a paper chromatogram run with the ethyl acetate – acetic acid – water (9:2:2 v/v) solvent, a strong spot (R_{gal} 1.4) corresponding to arabitol and a small one (R_{gal} 2.0) corresponding to lyxono-γ-lactone (ammoniacal silver nitrate spray). It crystallized and was recrystallized twice from ethyl acetate – methanol and then from ethanol. The crystals (72 mgm.), m.p. 99–101°C., $[\alpha]_D$ +7° (*c*, 11.0, saturated aqueous borax), undepressed on admixture with authentic D-arabitol, gave the same X-ray powder diagram as D-arabitol. Calculated for $C_5H_{12}O_5$: C, 39.47%, H, 7.95%; found: C, 39.43%, H, 7.99%.

*1,2-O-Isopropylidene-*D*-arabopenturonic Acid Methyl Ester*

The *arabo*penturonic acid – lactone mixture (145 mgm.) was shaken for 18 hr. in acetone (20 cc.) containing sulphuric acid (0.1 cc.). The solution was neutralized with barium carbonate, filtered, and evaporated to a white solid. The residue was dissolved in water, treated with Amberlite IR-120, and the solution evaporated to a sirup (178 mgm.). The product was dissolved in methanol and treated with ethereal diazomethane until the yellow color persisted. The solvents were evaporated off and the resulting sirup (192 mgm.) partly crystallized. The crystals were isolated and recrystallized from ether–pentane to give long colorless prisms (26 mgm.), m.p. 133–134°C., $[\alpha]_D$ +67°

(*c*, 1.0, ethanol); non-reducing to Fehling's solution. Calculated for $C_9H_{14}O_6$: C, 49.54%, H, 6.47%; found: C, 49.62%, H, 6.36%. The poor yield is probably accounted for by the small proportion of free D-*arabo*penturonic acid present in the starting material.

Methyl D-*Arabopentofururonoside Methyl Ester*

The sirup containing D-*arabo*penturonic acid and its lactone (291 mgm.) was dissolved in 0.5% methanolic hydrogen chloride (5 cc.) and refluxed for five minutes. The solution was neutralized (Ag_2CO_3) and evaporated to a sirup (339 mgm.), which did not reduce Fehling's solution. Distillation (bath temperature 140°C. at 1 mm.) gave the methyl ester glycoside as a sirup (83% of sirup distilled), n_D^{21} 1.4723, $[\alpha]_D$ +19° (*c*, 2.9, ethanol). Calculated for $C_7H_{12}O_6$: C, 43.75%, H, 6.29%, –OMe, 32.3%; found: C, 44.10%, H, 6.23%, –OMe, 33.3%.

D-*Arabopenturonic Acid*

The methyl ester methyl fururonoside (127 mgm.) was converted to D-*arabo*penturonic acid by heating at 100°C. for 10 hr. in water (2 cc.) containing formic acid (0.2 cc.). The solution was evaporated to a sirup (105 mgm.), $[\alpha]_D$ +22° (*c*, 2.6, water), which gave on a paper chromatogram (acid solvent) a gray-brown spot with R_{rh} 0.42 using the *p*-anisidine hydrochloride spray.

D-*Lyxono-γ-lactone*

D-*Arabo*penturonic acid obtained by acid hydrolysis of its methyl ester methyl fururonoside (134 mgm.) was dissolved in water (10 cc.) and added to an aqueous solution (10 cc.) of sodium borohydride (250 mgm.). After 18 hr. the reaction mixture was worked up as in the preparation of arabitol (above) and the final sirup was heated at 100°C. for six hours to promote lactonization. On a paper chromatogram (neutral solvent; ammoniacal silver nitrate spray) the product showed mainly lyxono-γ-lactone and a trace of material corresponding to arabitol. The sirup crystallized and it was recrystallized thrice from ethyl acetate. Yield 23 mgm., m.p. and mixed m.p. 108–110°C., and $[\alpha]_D$ +70° (*c*, 4.0, water). The product gave an X-ray diffraction pattern similar to that of D-lyxono-γ-lactone. Calculated for $C_5H_8O_5$: C, 40.54%, H, 5.44%; found: C, 40.67%, H, 5.49%.

D-*Arabinose*

The distilled methyl ester of methyl-D-*arabo*pentofururonic acid (158 mgm.) in ice cold water (10 cc.) was added during 10 min. to ice cold aqueous sodium borohydride (200 mgm. in 10 cc.). After 18 hr. at 0°C. and 10 hr. at 27°C. the reduction product was isolated as in the preparation of arabitol and the free carboxyl groups were esterified with ethereal diazomethane. A second treatment of the methyl ester with sodium borohydride was then carried out. The final product was dissolved in water, passed through IR4B to remove the unchanged acid, and evaporated to a sirup (116 mgm.). On a paper chromatogram (neutral solvent) it moved with R_{rh} 1.2 (spray: ammoniacal silver nitrate). On detection with the *p*-anisidine hydrochloride spray a pink spot of similar speed was observed. It corresponded to methyl-αβ-arabofuranoside.

The methyl-$\alpha\beta$-D-arabofuranoside (116 mgm.) was hydrolyzed in water (4 cc.) containing formic acid (1 cc.) at 100°C. for two hours. The solution was evaporated to a sirup which was dissolved in water and kept at 100°C. for two hours to hydrolyze formate esters. On evaporation the sirup obtained (105 mgm.) was found by paper chromatography to contain only arabinose (neutral solvent; sprays: *p*-anisidine hydrochloride and ammoniacal silver nitrate). The sirup crystallized and the material was twice recrystallized from ethanol. Yield 30 mgm., m.p. *ca.* 147°C.

Since the melting point of the D-arabinose was low, it (16 mgm.) was refluxed for 30 min. in methanol (10 cc.) containing toluene-*p*-sulphonylhydrazine (1.2 equivalents; 24 mgm.). The product was recrystallized from methanol. Yield 10 mgm., m.p. and mixed m.p. 150–152°C. Calculated for $C_{12}H_{18}O_6N_2S$: C, 45.28%, H, 5.70%; found: C, 45.27%, H, 5.705%. The crystals gave an X-ray powder diagram which was identical with that of authentic D-arabinose toluene-*p*-sulphonylhydrazone.

D-Threotetruronic Acid

The rate of reaction of lead tetraacetate with D-galacturonic acid in acetic acid was followed in the manner described for the oxidation of D-glucurone. The following results were obtained:

Oxidation time (min.)	2	5	10	30	60	131
Molar uptake of lead tetraacetate	2.22	2.26	2.33	2.49	2.88	3.53

On a larger scale, D-galacturonic acid monohydrate (860 mgm.) in water (2 cc.) and acetic acid (100 cc.) was stirred vigorously with lead tetraacetate (3.6 gm.; 2 equivalents). After two minutes the solution had cleared and no oxidant remained. Water (100 cc.) was added followed by 10% oxalic acid in acetic acid (8.2 cc.). The precipitate which formed was filtered off with the aid of Celite and the filtrate was evaporated to a sirup which was dissolved in water (25 cc.). After 18 hr. the solution was passed through Amberlite IR-120 and the eluate evaporated to a friable light yellow solid (530 mgm.) with $[\alpha]_D$ $-11° \rightarrow +3°$ (18 hr.; constant value; *c*, 2.3, water). On a paper chromatogram (acidic solvent; spray: *p*-anisidine hydrochloride) a yellow-brown spot of R_{gal} 1.3 was obtained.

Formate Ester of D-Threotetruronic Acid

D-Galacturonic acid was oxidized with lead tetraacetate using the same amounts and conditions as above. Remaining excess lead was removed from the acetic acid solution by stirring with Amberlite IR-120 until no precipitate was produced on addition of oxalic acid in acetic acid. The mixture was evaporated to a sirup which was dissolved in ethyl acetate. A little insoluble material was separated by filtration and the filtrate was evaporated to a sirup which was kept overnight at 1 mm. pressure over potassium hydroxide. The product (497 mgm.) absorbed strongly in the infrared region at 1725 cm.$^{-1}$ and 1170 cm.$^{-1}$, characteristic of formate esters (1723 cm.$^{-1}$ and 1170–1200 cm.$^{-1}$) and was shown by saponification with alkali to contain 1.0 formate ester group, assuming a molecular weight of 162.

D-*Threotetruronic Acid 2,4-Dinitrophenylhydrazone*

The tetruronic acid (138 mgm.) was refluxed for 18 hr. in ethanol (40 cc.) containing 2,4-dinitrophenylhydrazine (204 mgm.; 1 equivalent) and acetic acid (1 cc.) and the solution was then evaporated to dryness. The residue was dissolved in warm aqueous ethanol from which crystals separated on cooling. Recrystallization from the same solvent gave ochre crystals (116 mgm.), m.p. 111–113°C. Calculated for $C_{10}H_{10}O_8N_4$: C, 38.22%, H, 3.21%; found: C, 37.99%, H, 3.165%.

D-*Threonic Acid Phenylhydrazide*

The tetruronic acid (140 mgm.) in water (10 cc.) was added to a solution of sodium borohydride (250 mgm.) in water (10 cc.). After 18 hr. reaction time the sirupy product (117 mgm.), isolated by the procedure described in the preparation of arabitol, was heated at 100°C. for eight hours in order to promote lactonization; it did not crystallize. On a paper chromatogram (neutral solvent; ammoniacal silver nitrate spray) the major spot had R_{rh} 1.3, and a fainter spot with R_{gal} <1, corresponding to unchanged acid, was also present. A portion of the sirup (58 mgm.) was refluxed for two minutes in ethanol (0.2 cc.) containing phenylhydrazine (36 mgm.) and then kept for 24 hr. at room temperature. The solution deposited crystals which were recrystallized from ethanol. Yield 15 mgm., m.p. 156–157.5°C. (D-erythronic acid phenylhydrazide (14) has m.p. 128°C.), and $[\alpha]_D$ −35° (*c*, 4.2, ethanol). Calculated for $C_{10}H_{14}O_4N_2$: C, 52.93%, H, 6.21%; found: C, 53.09%, H, 6.24%.

D-*Threotetruronic Acid Methyl Ester Dimethyl Acetal*

The tetruronic acid (201 mgm.) was refluxed for two minutes in 1% methanolic hydrogen chloride (10 cc.) and allowed to stand at room temperature for 18 hr. The solution was neutralized (Ag_2CO_3), filtered, and evaporated to a sirup which was distilled (bath temperature 120°C. at 1 mm.). The resulting sirup (177 mgm.) had $[\alpha]_D$ −27° (*c*, 2.3, ethanol) and n_D^{21} 1.4501. Calculated for $C_7H_{14}O_6$: C, 43.29%, H, 7.27%, $-OCH_3$, 46.9%; found: C, 43.42%, H, 7.25%, $-OCH_3$, 46.2%.

D-*Erythrotetruronic Acid*

The rate of oxidation of potassium D-glucuronate with $Pb(OAc)_4$ in acetic acid was followed using the method described for the oxidation of D-glucurone. The following results were obtained:

Oxidation time (min.)	2	4	7	15	22
Molar uptake of lead tetraacetate	1.92	2.16	2.37	2.53	2.62

Potassium D-glucuronate (1.76 gm.) in water (2 cc.) was mixed with acetic acid (200 cc.), and lead tetraacetate (7.4 gm.; 2.2 equivalents) added with vigorous stirring. When the lead tetraacetate had dissolved, water (200 cc.) was added followed by 10% oxalic acid in acetic acid (17.6 cc.). The precipitate was filtered off, and the filtrate evaporated to a sirup which was dissolved in water (25 cc.). After 18 hr. the solution was passed through Amberlite IR-120 and the eluate evaporated to a sirup (516 mgm.), $[\alpha]_D$ +16° → +18° (18 hr.;

constant value; *c*, 2.32, water). On a paper chromatogram (acidic solvent; *p*-anisidine hydrochloride spray) the main spot was yellow-brown, with R_{gal} 1.4 and also there was a reddish brown spot of R_{rh} 1.3.

D-*Erythrono-γ-lactone*

The tetruronic acid (106 mgm.) was reduced with aqueous sodium borohydride as described for the preparation of D-threonolactone from D-*threo*-tetruronic acid. The sirupy product (93 mgm.) crystallized after distillation (1 mm. pressure). The distillate, on a paper chromatogram (neutral solvent; ammoniacal silver nitrate spray), gave a single spot corresponding to erythrono-γ-lactone. The crystals were separated by tiling and were recrystallized twice from benzene–ethanol. Yield 7 mgm., m.p. 99–102°C., $[\alpha]_D$ +73° (*c*, 1.3, water). Calculated for $C_4H_6O_4$: C, 40.68%, H, 5.12%; found: C, 40.73%, H, 5.19%. The X-ray diffraction pattern of the product was identical with that of D-erythrono-γ-lactone.

D-*Erythrotetruronic Acid Methyl Ester Dimethyl Acetal*

The sirupy tetruronic acid (230 mgm.) was dissolved in 1% methanolic hydrogen chloride (5 cc.) which was then refluxed for a few seconds and left at 27°C. for 24 hr. The solution was neutralized (Ag_2CO_3), filtered, and evaporated to a sirup which was distilled at 1 mm. pressure (bath temperature 120°C.) to give a sirup (175 mgm.), n_D^{21} 1.4557 and $[\alpha]_D$ +40° (*c*, 2.7, ethanol). Calculated for $C_7H_{14}O_6$: C, 43.29%, H, 7.27%, $-OCH_3$, 46.9%; found: C, 43.27%, H, 7.23%, $-OCH_3$, 46.9%.

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FREE RADICALS BY MASS SPECTROMETRY

XI. THE MERCURY PHOTOSENSITIZED DECOMPOSITION OF C_2–C_4 OLEFINS[1]

By F. P. Lossing, D. G. H. Marsden,[2] and J. B. Farmer[2]

ABSTRACT

The mercury photosensitized (Hg^3P_1) decomposition of olefins has been examined using a reactor coupled directly to a mass spectrometer. The primary split of ethylene has been shown to be predominantly molecular, and that of propylene mainly into an allyl radical and a hydrogen atom. With 1-butene the split is predominantly at a C–C bond giving allyl and methyl radicals, although a rupture of a C–H bond occurs as well. With 2-butene and isobutene a C–H bond is broken. It is concluded that the allyl and methallyl radicals produced have large cross sections for reaction with excited mercury atoms.

INTRODUCTION

The use of mass spectrometers to detect free radicals in reacting systems has been described by a number of authors and has been reviewed in some detail in two recent publications (24, 26). The radicals have been produced by various means: pyrolysis in furnaces and on hot filaments, by reactions of hydrogen atoms, and in combustion flames. Although some 25 free radicals have been detected in pyrolytic reactions, the temperatures used in the production of the radicals are usually so high that only radicals with considerable thermal stability can be studied. In addition, the reactions of such radicals that are stable enough to be investigated are those corresponding to much higher temperatures than are customary in kinetic studies. It would be a great advantage if a means of producing radicals at lower temperatures could be employed.

NH_2 radicals and CN radicals have been detected in a continuously irradiated flow system by photographing the absorption spectrum (23). The absorption coefficients of most organic compounds are so small, however, that at low pressures very little energy is absorbed by a reactant which is flowing rapidly through an illuminated zone of reasonable proportions. The use of external reflectors to increase the path length is of little advantage at these pressures since the wall of the reaction vessel absorbs much more radiation than the reactant.

This difficulty could be overcome in part by taking advantage of the large absorption coefficient of mercury vapor for radiation of 2537 Å, as has been done in studies of photosensitized reactions. Preliminary work (8) has shown that mercury photosensitization permits the absorption of sufficient quanta to dissociate acetone in a fast flow system. At a partial pressure of a few microns in a stream of helium at 8 mm., acetone was dissociated to the extent of 50–80% in 0.002 sec. The detection of CH_3CO radicals as well as CH_3 radicals showed that relatively unstable radicals could be produced in appreciable amounts.

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[2]*National Research Council of Canada Postdoctorate Fellow.*

In the present work an attempt has been made to use this technique to determine the primary products of dissociation of C_2–C_4 olefins upon collision with $Hg(^3P_1)$ atoms. The reaction conditions are much different from those ordinarily used in photosensitized studies, the partial pressure of reactant being only a few microns and the partial pressure of mercury much higher. The incident flux is greater than is customary. A large excess of helium is present. These factors make conditions more favorable for determining the primary step, but the subsequent reaction products may be quite different from those found at higher pressures and lower intensities.

Previous work on the photosensitized decomposition of olefins has been reviewed in detail (17, 26) and only a brief summary will be given here.

For ethylene a molecular split has been suggested (28) and a mechanism involving an excited ethylene molecule has been proposed (18):

$$C_2H_4 + Hg(^3P_1) \rightarrow C_2H_4^* + Hg(^1S_0) \quad [1]$$

$$C_2H_4^* \rightarrow C_2H_2 + H_2 \quad [2]$$

$$C_2H_4^* + C_2H_4 \rightarrow 2C_2H_4. \quad [3]$$

An alternative primary split is one leading to a vinyl radical and H atom (16):

$$C_2H_4 + Hg(^3P_1) \rightarrow C_2H_3 + H + Hg(^1S_0). \quad [4]$$

Evidence for the occurrence of reaction [4] has been found at 300°C. (19) but at lower temperatures the evidence supports the split by reactions [1] and [2]. The predominance of reactions [1] and [2] over reaction [4] has been recently demonstrated quite convincingly using mixtures of C_2H_4 and C_2D_4 (2, 4). There is evidence that the detailed reaction is more complex than written above (5, 2, 3).

The mercury photosensitized decomposition of propylene appears to proceed by the following mechanism (10):

$$C_3H_6 + Hg(^3P_1) \rightarrow C_3H_6^* + Hg(^1S_0) \quad [5]$$

$$C_3H_6^* \rightarrow C_3H_5 + H \quad [6]$$

$$C_3H_6^* + C_3H_6 \rightarrow 2C_3H_6. \quad [7]$$

The absence of an initial pressure rise led these authors to the conclusion that reaction [6] predominated over the analogue of reaction [2], presumably as a result of the weaker C–H bond in propylene. Although the quenching cross-section for propylene is slightly larger than for ethylene (6) the quantum yield is only about one-half that of ethylene (26).

The mercury photosensitized decompositions of the butenes have not been studied in as much detail. The main products of the reaction of 1-butene were 2-butene and a liquid polymer (12). At low pressures other products were found and the following mechanism was proposed:

$$1\text{-}C_4H_8 + Hg(^3P_1) \rightarrow 1\text{-}C_4H_8^* + Hg(^1S_0) \quad [8]$$

$$1\text{-}C_4H_8^* \rightarrow C_4H_7 + H \quad [9]$$

$$1\text{-}C_4H_8^* + 1\text{-}C_4H_8 \rightarrow 2\text{-}C_4H_8 + 1\text{-}C_4H_8. \quad [10]$$

The reaction of $Hg(^3P_1)$ atoms with 2-butene was found to be similar except that no isomerization to 1-C_4H_8 occurred (12). In the mercury photosensitized reaction of isobutene, a complex mixture of products was found (11, 1) and the following mechanism was suggested:

$$\text{iso-}C_4H_8 + Hg(^3P_1) \rightarrow \text{iso-}C_4H_8^* + Hg(^1S_0) \quad [11]$$

$$\text{iso-}C_4H_8^* \rightarrow \text{products} \quad [12]$$

$$\text{iso-}C_4H_8^* + \text{iso-}C_4H_8 \rightarrow 2\ \text{iso-}C_4H_8. \quad [13]$$

The nature of the products of reaction [12] could not be determined. A liquid polymer was found and was attributed to the following reaction:

$$\text{iso-}C_4H_8^* + \text{iso-}C_4H_8 \rightarrow C_8H_{16}. \quad [14]$$

EXPERIMENTAL

The Reactor

A diagram of the reaction system used is given in Fig. 1. It consisted of a mercury saturator, a reaction zone, and a low pressure mercury lamp. The

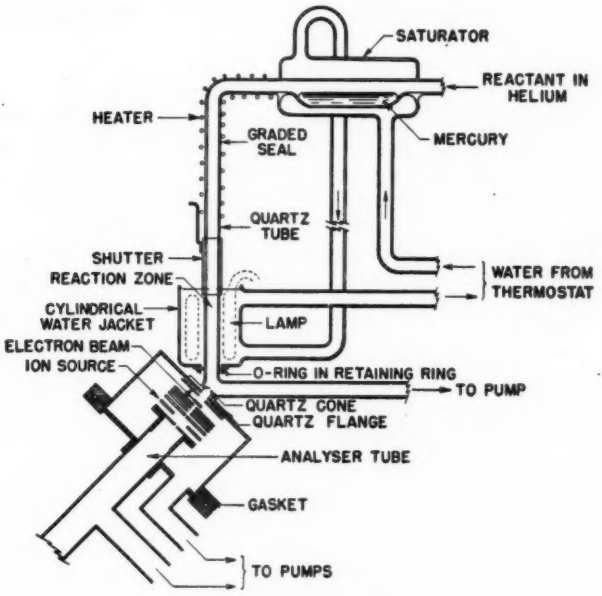

FIG. 1. The reaction system.

reactant gas, at a partial pressure of a few microns, was carried in a stream of helium at about 8 mm. pressure through the mercury saturator into the reaction zone. Just beyond the reaction zone the gas stream passed over a quartz cone containing a small orifice opening into the ionization chamber of a mass spectrometer. A suitable rate of flow was obtained by a pump of large capacity.

The reactor itself was constructed of a length of quartz tubing of 7 mm. inside diameter bent into a right angle. At the elbow thus formed a larger tube of quartz, suitably drawn down, was sealed. This tube was cut off and flared out to form a flange with a central hole, into which was sealed a quartz cone of the type described previously (21). The tip of this cone, which had been pierced by a spark to form a circular hole 28μ in diameter, projected about 2 mm. into the reactor tubing. By means of the flange, the reactor was cemented to the top of the vacuum jacket of the mass spectrometer tube with Apiezon W wax. This seal was sufficiently soft to prevent breakage of the quartz by differential expansion. A copper cooling coil (not shown in Fig. 1) soldered to the top of the vacuum jacket prevented the wax from becoming too soft during outgassing of the tube, or as a result of heating by the mercury lamp.

The Mercury Lamp

Since a high intensity of unreversed 2537 Å radiation was required to produce sufficient decomposition of reactant in a contact time of a millisecond, special consideration was given to the design of the low pressure mercury lamp. A number of designs, consisting of helices of quartz of various internal diameters, were tried, but all were inferior to the design shown in Fig. 2.

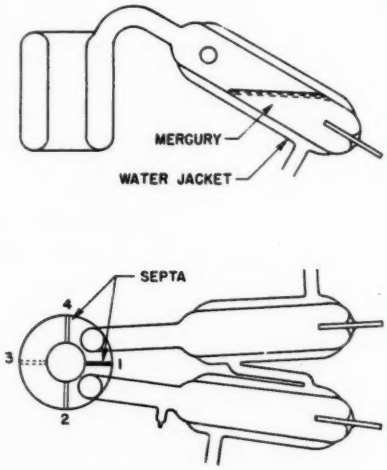

FIG. 2. The mercury lamp.

The body of the lamp consisted of two concentric cylinders of quartz tubing with internal diameters of 13 mm. and 23 mm. These were sealed together at the top and bottom to form an annular cell 36 mm. long. Four longitudinal septa were provided as shown in Fig. 2, the septa numbered 2 and 4 having a space at the bottom and that numbered 3 having a space at the top. Septum No. 1 extended the full length of the cell. The discharge was in this way forced to proceed in a zigzag path which filled the cell almost completely. The electrodes were water-cooled mercury pools. After being thoroughly

outgassed by heating, the lamp was filled with neon at a pressure of 1.5 mm. When operated from a source of 220 v. d-c. through a series resistor the lamp was started by being touched with a Tesla coil. At a current of 4–5 amp. the voltage drop across the lamp was 90 v. To prevent self-reversal the body of the lamp and the electrodes required water cooling. Conditions for the maximum output of unreversed 2537 Å radiation could be rapidly determined by observing the extent of decomposition of ethylene flowing through the reactor. The maximum output was found to occur with the electrodes at about 10°C. and the body of the lamp at 55–60°C. It was found, rather surprisingly, that the partial pressure of mercury in the lamp was not determined by the temperature of the mercury pool electrodes. Even with the electrodes at 10°C. and the body of the lamp at 60°C., mercury slowly condensed in the latter. Evidently the pumping action of the current was able to overcome the rate of diffusion. It is interesting to note that the temperature of optimum output agrees quite well with that of 50°C. found for a low pressure lamp with iron electrodes (14) although the criterion for maximum output was not the same. In the present work only the unreversed 2537 Å line was effective, while in the work of Heidt and Boyles the output was measured by uranyl oxalate actinometry, which would respond to the wings of the line as well.

The vapor pressure of mercury at 60°C. is 25.2μ and with this partial pressure in the reactor the absorption of the 2537 Å line was probably complete in the 7 mm. diameter of the reactor tube. Owing to the rapid deposit of polymeric layers on the reactor at high reactant pressures it was not possible to measure the amount of ethylene decomposed under conditions of complete quenching. It was found, however, that a quantity of ethylene greater than that equivalent to 1.39 cc. (the illuminated volume) at 0.010 mm. could be decomposed in 0.001 sec., i.e. about 5×10^{17} molecules/sec. It is probable that the output of unreversed 2537 Å radiation falling on the reaction volume of 1.39 cc. was in excess of 10^{18} photons/sec., an amount roughly the same as that found by Heidt and Boyles.

The Water Circulating System

The arrangement shown in Fig. 1 for maintaining the body of the lamp and the reactor at 60°C. was found to be convenient. A cylindrical Pyrex water jacket was made with a hole in the bottom slightly larger than the outside diameter of the reactor tubing. A Pyrex retaining ring cemented over the hole served to hold a rubber O-ring, making a watertight seal around the reactor tube. This allowed the lamp and water jacket to be slid upward along the reactor tube so that the reactor could be cleaned by heating with a torch when polymeric deposits in the reactor reduced the transparency. Flowing oxygen through the reactor while flaming removed the most stubborn deposits.

Water connections to the mercury saturator and the thermostat were made by means of ball and socket ground joints which could be removed to allow the water jacket to be moved. It was found that contact of the cooling water with metal parts caused an opaque deposit to be formed on the lamp. Consequently distilled water was used, and the thermostat and connecting tubing

were also made of glass. A glass centrifugal pump provided sufficient pressure to pump water through the jacket of the mercury saturator to the water jacket. The overflow from the latter returned to the thermostat. When the lamp was operating, the temperature of the reactor was a degree or so higher than that of the saturator. This served to prevent condensation of mercury in the reactor.

The Gas Flow System

The control of the helium flow and the addition of reactants at a constant proportion was the same as that described previously (20). Using a mechanical pump with a free air capacity of 140 liters/min., a flow through the reactor of 50–60 meters/sec. could be obtained with helium pressures of from 7 to 13 mm. The rate of flow was adjusted over the range of 10–60 meters/sec. by means of taps of various size in the pumping lead.

The Mass Spectrometer and Operation

The mass spectrometer has been described in earlier papers of this series (21, 20). The identification of the free radicals was done by the low electron energy method of Eltenton (7). In some cases the long periods of illumination required for the complete scanning of spectra at 50 v. resulted in the formation of sufficient polymer in the reactor to change the fraction of reactant decomposed during the time of scanning. This frequently interfered with the measurement of the spectra of the reaction products.

It has been assumed throughout this work that the appearance of a given ion at an electron energy appreciably less than that required to produce the ion from any identifiable stable compound present indicated the presence of a free radical with this mass. Where possible the identification was supplemented by a search for the corresponding dimerization product. It is, of course, possible that the appearance potential of a given ion from an excited molecule such as $C_3H_6^*$ or $C_4H_8^*$ might be lower than the normal appearance potential. It seems reasonable to suppose that in such an excited molecule the appearance potentials of all ions would be lowered by a similar amount. If this were detectable by the present apparatus it would lead to the spurious detection of "free radicals" of a mass number corresponding to each ionic species formed by electron impact on the excited molecule. No such effect was found in the present apparatus. The lifetimes of such excited molecules are short compared to those of free radicals, and an insignificant fraction would survive long enough to be struck by an electron.

Detection of H Atoms

A difficulty arose in the detection of hydrogen atoms produced in some of the reactions studied. In experiments in which hydrogen was reacted with Hg ($^3P_1$) atoms, the amount of reaction was much less than expected, H atoms being detected only in small amounts. It was concluded that the combination of H atoms to H_2 occurred rapidly, most probably on the walls of the ionization chamber. Consequently, a failure to detect H atoms among the products of decomposition of a compound was not a proof that they were not formed. On the other hand the formation of H_2 by reactions such as

$$H + RH \rightarrow H_2 + R \qquad [15]$$

is undoubtedly too slow at 60°C. to form appreciable quantities of H_2 under the reaction conditions used. In earlier work with CH_3 radicals (15) it was found that even at 850°C. a small amount of methane found among the products of decomposition of mercury dimethyl did not arise from reactions such as

$$CH_3 + RH \rightarrow CH_4 + R \qquad [16]$$

but rather from reactions in the ion source. For this reason the formation of H_2 by reaction [15] at 60°C. was considered to be negligible.

Contact Times

In almost all the experiments described a standard pressure of helium of 7.8 mm. was used. The contact time was varied either by changing the pumping speed, or more conveniently by reducing the length of the illuminated zone by a cylindrical shutter of tantalum (Fig. 1).

RESULTS AND DISCUSSION

Ethylene

In the photosensitized decomposition of ethylene the only products of any importance were acetylene and hydrogen. No other products were found in the mass range 2–100 except for small peaks (~0.5% of C_2H_2 peaks) at mass 52 and 50. No radicals could be detected at mass 27 and no butadiene was formed. The extent of decomposition and the yields of hydrogen and acetylene for a typical experiment are given in Table I. The carbon balance has an

TABLE I

PHOTOSENSITIZED DECOMPOSITION OF ETHYLENE

C_2H_4 pressure (μ)		C_2H_4 reacted		Contact time (millisec.)	C_2H_2 found		H_2 found	
Lamp off	Lamp on	μ	%		μ	Yield (%)	μ	Yield (%)
3.03	1.78	1.25	41.3	1.4	1.27	102	1.06	85

estimated error of 5% and the hydrogen balance is considerably more uncertain. It may be concluded that vinyl radical production, if it occurred, amounted to less than 3% of the total reaction. Experiments with higher pressures of ethylene also showed no sign of vinyl radical production. In a separate experiment in which acetylene was irradiated it was found to decompose hardly at all in the same contact time, so that no secondary reactions would be expected. These results constitute good evidence for a molecular process for the decomposition of ethylene at 60°C., and are in agreement with the recent experiments of Cvetanović and Callear (2, 4) in this respect.

Propylene

Under the same experimental conditions as with ethylene, the decomposition of propylene led to the formation of allyl radicals in considerable amounts as shown by a search at low electron energies. The dimer of allyl, 1,5-hexadiene, was also produced. Other products were allene in appreciable quantity, and traces of ethylene and acetylene. Since the mass spectrum of the allyl radical

in the mass 40 range was not determined, a quantitative measurement of the amount of allene could not be made and a carbon balance was not obtained. The extent of decomposition and the yield of hydrogen (presumably from H atom combination) are shown in Table II. It was possible to show in the following way that allene was produced mainly by a secondary reaction. At an electron energy of about 10 v., the mass 40 (allene) and 41 (allyl) peaks were free from contributions from other compounds and the ratio of their heights was proportional (but not equal) to the ratio of allene and allyl present. As the contact time was shortened by using the shutter, it was observed that the amount of allene decreased greatly while the amount of allyl decreased only slightly (Table II). A large decrease in allene production

TABLE II

PHOTOSENSITIZED DECOMPOSITION OF PROPYLENE

C_3H_6 pressure (μ)		C_3H_6 reacted		Contact time	H_2 found		Mass	Mass	Ratio
Lamp off	Lamp on	μ	%	(millisec.)	μ	Yield (%)	40	41	40/41
1.40	1.16	0.24	17.1	1.4	0.21	88	—	—	—
1.36	1.22	0.14	10.3	0.7	0.11	79	—	—	—
Low electron energy experiments				0.7	—	—	0.40	0.70	0.57
				0.4	—	—	0.10	0.62	0.16
				0.2	—	—	0.05	0.55	0.09

would be expected if it were produced from allyl by a secondary process, but not if it were produced in a primary molecular split of propylene. The relatively small decrease in the amount of allyl shows that the decrease in production resulting from the shorter contact time was nearly balanced by the decrease in reactions removing allyl. The high yield of hydrogen (Table II) indicates that the fate of most of the allyl radicals was to give a hydrogen atom. This also supports the view that allyl radicals were disappearing rapidly to form allene and an H atom. Three reactions by which this could occur may be considered:

$$CH_2{:}CH{\cdot}\dot{C}H_2 + H \rightarrow CH_2{:}C{:}CH_2 + H_2 \qquad [17]$$

$$CH_2{:}CH{\cdot}CH_2^* \rightarrow CH_2{:}C{:}CH_2 + H \qquad [18]$$

$$CH_2{:}C\dot{H}{\cdot}\dot{C}H_2 + Hg(^3P_1) \rightarrow CH_2{:}C{:}CH_2 + H + Hg(^1S_0). \quad (\text{or } HgH) \qquad [19]$$

Reaction [17] is undoubtedly too slow at 60°C. to be effective. Such abstraction reactions are several orders of magnitude slower than dimerizations, and only a small proportion of allyl radicals had time to dimerize. The second reaction is improbable on energetic grounds. Of the 112 kcal. imparted by a $Hg(^3P_1)$ atom, about 77 kcal. (27) are required to break the $CH_2{:}CH{\cdot}CH_2$–H bond. The allyl radicals could have a maximum excitational energy of 35 kcal., neglecting the translational energy imparted to the H atom. From the heat of formation of allene, 45.9 kcal./mole at 25°C. (25), and of allyl, 32 kcal./mole (22), a dissociation energy of 65 kcal./mole can be derived for the C_3H_4–H bond in allyl. Even if this value were in error by more than a few kilocalories there is not sufficient energy available for a "hot" allyl to dissociate.

The third possibility, reaction [19], is generally not considered in conventional photosensitized reaction experiments because of the relatively low concentrations of radicals and excited mercury atoms. In the present work, however, the high intensity of radiation and the low pressure of olefin results in relatively large concentrations of radicals and excited mercury atoms, and collisions between these are not statistically negligible. It should be noted from the reactions given below that if reaction [19] did not occur, the yield of H_2 would be 50%, and if all allyl radicals were removed by this reaction, the yield would be 100%. A yield of 79%, as found, indicates that some $2\times(79-50)$ or 58% of the radicals had decomposed in this way. Since propylene itself was decomposed to the extent of 10.3% in a somewhat greater contact time, it would appear, if this interpretation is correct, that allyl radicals have a cross section for reaction with $Hg(^3P_1)$ atoms about five times larger than has propylene. This could arise from a larger collision cross section for quenching or a larger quantum yield, or from a combination of both.

On this basis the following reactions would account for the products found:

$$CH_2{:}CH{\cdot}CH_3 + Hg(^3P_1) \rightarrow CH_2{:}CH{\cdot}\dot{C}H_2 + H + Hg(^1S_0) \quad [20]$$

$$CH_2{:}CH{\cdot}\dot{C}H_2 + Hg(^3P_1) \rightarrow CH_2{:}C{:}CH_2 + H + Hg(^1S_0) \quad [19]$$

$$2CH_2{:}CH{\cdot}\dot{C}H_2 \rightarrow \text{1,5-hexadiene} \quad [21]$$

$$H + H + M \rightarrow H_2 + M. \quad [22]$$

The present work gives no direct indication as to whether reactions [20] and [19] proceed by formation of HgH or by excited molecule formation. As mentioned above, a large part of reaction [22] must proceed in the ion source.

Isobutene

The extent of decomposition of isobutene under the same experimental conditions as used with propylene and ethylene is given in Table III, along

TABLE III

PHOTOSENSITIZED DECOMPOSITION OF ISOBUTENE

Isobutene pressure (μ)		Isobutene decomposed		Contact time (millisec.)	H_2 found	
Lamp off	Lamp on	μ	%		μ	Yield (%)
1.75	1.57	0.18	10.4	1.4	0.10_1	56.0
1.72	1.61	0.11	6.5	0.7	0.05_6	50.0

with the yield of H_2 based on the isobutene decomposed. A search for radicals at low electron energy showed that a radical of mass 55 was produced in considerable amounts, and that methyl radicals were present in small amounts. Allene, an octadiene, and a pentene were also produced. The spectrum of the octadiene was similar to that of 2,5-dimethyl-1,5-hexadiene, the dimer of the β-methallyl radical (22). Of the two possible radicals of mass 55 which could be formed from isobutene

$$\dot{C}H{:}C{\cdot}CH_3 \quad \text{and} \quad CH_2{:}C{\cdot}\dot{C}H_2$$
$$\quad\dot{C}H_3 \qquad\qquad\quad \dot{C}H_3$$

the second (β-methallyl) is capable of resonance stabilization because of its allylic structure, and the β-methallyl–H bond is correspondingly weak, 76 ± 3 kcal./mole (22). From this consideration and from the identity of the dimer, it is almost certain that the radical formed is β-methallyl. Considering the structure of isobutene, neither methyl radicals nor allene appear to be likely products of a primary split. They have, however, been identified as the products of thermal decomposition of β-methallyl radicals (22). In view of this it is reasonable to believe that they arise from the reaction of a β-methallyl radical with a $Hg(^3P_1)$ atom, in a manner analogous to reaction [19]. As with propylene, the decomposition of a radical carrying excitation energy left over from the primary split is unlikely on energetic grounds. From the heat of formation of allene, 45.9 kcal./mole (25), and that of β-methallyl radical, 21.3 ± 3 kcal./mole (22), and methyl radical, 32.6 kcal./mole (13), the dissociation energy of the C_3H_4–CH_3 bond in β-methallyl radical is 57 kcal./mole. From ΔH_f(isobutene) $= -3.3$ kcal./mole (25) and ΔH_f(β-methallyl) as above, D(β-methallyl–H) $= 76$ kcal./mole. Consequently the maximum excitation of a "hot" β-methallyl would be only 36 kcal.

The reactions which would account for the products found are then:

$$CH_2{:}C(CH_3)CH_3 + Hg(^3P_1) \rightarrow CH_2{:}C(CH_3)\dot{C}H_2 + H + Hg(^1S_0) \quad [23]$$

$$CH_2{:}C(CH_3)\dot{C}H_2 + Hg(^3P_1) \rightarrow CH_2{:}C{:}CH_2 + CH_3 + Hg(^1S_0) \quad [24]$$

$$2CH_2{:}C(CH_3)\dot{C}H_2 \rightarrow \text{2,5-dimethyl-1,5-hexadiene} \quad [25]$$

$$CH_3 + CH_2{:}C(CH_3)\dot{C}H_2 \rightarrow C_5H_{10} \quad [26]$$

$$H + H + M \rightarrow H_2 + M. \quad [22]$$

These reactions would lead to a yield of H_2 of 50%, in good agreement with that found (Table III). In addition to these products small amounts of propylene and a substance of mass 54 were found. It is difficult to understand how either of these products could be produced either as a primary reaction or by secondary reactions among the species identified. The formation of butadiene (mass 54) appears improbable since an extensive rearrangement would be required. One possible origin of a substance of mass 54 would be the removal of a hydrogen from β-methallyl to form methylene cyclopropane:

$$CH_2{:}\underset{\displaystyle CH_3}{\underset{|}{C}}\!-\!\dot{C}H_2 + Hg(^3P_1) \rightarrow CH_2{:}C\!<\!\begin{matrix}CH_2\\ CH_2\end{matrix} + H + Hg(^1S_0). \quad [27]$$

The preparation of methylene cyclopropane has been carried out (9) by removal of chlorine as follows:

$$CH_2{:}\underset{\displaystyle CH_2Cl}{\underset{|}{C}}\!-\!CH_2Cl \xrightarrow{Mg} CH_2{:}C\!<\!\begin{matrix}CH_2\\ CH_2\end{matrix} \quad [28]$$

This reaction is essentially similar to reaction [27].

The primary split, reaction [23], is the same as that suggested by previous workers (11) although the final products of the reaction are quite different.

The products also differ from those found by Allen and Gunning (1). This is to be expected in view of the great difference in the isobutene pressure in the two experiments. The latter authors found evidence for excited molecule formation and it is probable that reaction [23] proceeds by this means. The dimer found by these authors may have been at least partly 2,5-dimethyl-1,5-hexadiene rather than a dimer of isobutene as they suggested.

2-Butene

In the photosensitized decomposition of 2-butene, a radical of mass 55, presumably the γ-methallyl radical $CH_3 \cdot CH{:}CH \cdot \dot{C}H_2$, was produced in considerable amounts. Other products were butadiene, hydrogen, some propylene, and possibly some allene. A dimer was also produced, whose spectrum was similar to the spectrum of 2,6-octadiene produced from γ-methallyl radicals previously (22). As no pure sample of 2,6-octadiene was available,

TABLE IV

PHOTOSENSITIZED DECOMPOSITION OF 2-BUTENE

2-Butene pressure (μ)		2-Butene decomposed		Contact time	H_2 found		Mass 54	Mass 55	Ratio
Lamp off	Lamp on	μ	%	(millisec.)	μ	Yield (%)	(low *E*)	(low *E*)	54/55
1.68	1.48	0.20	11.9	1.4	0.17	85.0	1.9	1.10	1.70
1.68	1.59	0.11	6.5	0.7	0.09_2	83.6	1.0	0.90	1.10

this identification was not completely certain. In order to establish whether butadiene was a primary product, the ratio of the 54 to 55 peaks at low electron energy was examined at different contact times. The ratio decreased but not as greatly as in the similar experiments with propylene. There is a possibility that some butadiene may be formed from 2-butene by a molecular process as well as by the decomposition of γ-methallyl radicals. As in the case of isobutene, the further decomposition of a "hot" radical can be ruled out. The dissociation energy of the γ-methallyl–H bond has been given as 80±3 kcal./mole (22) and the maximum excitation of the radical could be 32 kcal. From ΔH_f(butadiene) = 26.3 kcal./mole (25) and ΔH_f(γ-methallyl radical) = 26±3 kcal./mole (22), the butadiene–H bond in γ-methallyl radical would be 52 kcal./mole. Insufficient energy would be available for a "hot" radical to decompose spontaneously.

1-Butene

The extent of decomposition of 1-butene and the yield of hydrogen are shown for two contact times in Table V. A search at low electron energy showed that allyl and methyl radicals were present in abundance and a radical of mass 55 in moderate amounts. Other products were allene, 1,5-hexadiene, ethane, hydrogen, and small amounts of pentene, butadiene, and propylene. With higher pressures peaks at mass 91, 95, and 96 appeared, suggesting the presence of a heptadiene. Experiments using the shutter indicated that allyl,

TABLE V

PHOTOSENSITIZED DECOMPOSITION OF 1-BUTENE

1-Butene pressure (μ)		1-Butene decomposed		Contact time (millisec.)	H_2 found	
Lamp off	Lamp on	μ	%		μ	Yield (%)
2.42	1.87	0.55	22.7	1.4	0.17	31
2.43	2.08	0.35	14.4	0.7	0.10	29

methyl, and the radical of mass 55 were primary products. The latter was undoubtedly a methallyl radical, the two forms $CH_2{:}CH\cdot\dot{C}H\cdot CH_3$ (α) and $\dot{C}H_2\cdot CH{:}CH\cdot CH_3$ (γ) being resonance hybrids.

The spectra given in Fig. 3 illustrate the detection of the allyl and methallyl radicals formed from 1-butene. Fig. 3A shows a portion of the low electron energy spectrum of 1-butene with the lamp off. With the lamp on and the shutter completely withdrawn (Fig. 3B) the increase in the mass 40, 41, and 42 peaks shows the presence of allene, allyl, and propylene. With the shutter halfway in, as in Fig. 3C, the contact time was halved, and the propylene and allene peaks were greatly reduced, while the allyl peak remained almost unchanged. This shows that allene and propylene were products of secondary reactions. In Fig. 3D the spectrum was obtained at an electron energy low enough to avoid the formation of the $C_4H_7^+$ ion (mass 55) by electron impact. With the lamp on (Fig. 3E) and the shutter withdrawn, the increase in the mass 54 and 55 peaks indicates the presence of butadiene and methallyl radicals. With the shutter halfway in (Fig. 3F), the butadiene peak was considerably reduced, while the methallyl peak was only slightly changed. Fig. 3G shows the 50 v. spectrum of the dimers 1,5-hexadiene at mass 82, 81, and 67; pentene at mass 70; and peaks at 96, 95, and 91, possibly heptadiene, barely visible.

The formation of the methyl, allyl, and methallyl radicals as primary products indicates that two modes of splitting must occur as primary steps:

$$CH_2{:}CH\cdot CH_2\cdot CH_3 + Hg(^3P_1) \rightarrow CH_2{:}CH\cdot\dot{C}H_2 + CH_3 + Hg(^1S_0) \quad [29]$$

$$CH_2{:}CH\cdot CH_2\cdot CH_3 + Hg(^3P_1) \rightarrow CH_2{:}CH\cdot\dot{C}H\cdot CH_3 + H + Hg(^1S_0). \quad [30]$$

The other products can be accounted for by the following reactions:

$$CH_2{:}CH\cdot\dot{C}H_2 + Hg(^3P_1) \rightarrow CH_2{:}C{:}CH_2 + H + Hg(^1S_0) \quad [31]$$

$$CH_2{:}CH\cdot\dot{C}H\cdot CH_3 + Hg(^3P_1) \rightarrow CH_2{:}CH\cdot CH{:}CH_2 + H + Hg(^1S_0) \quad [32]$$

$$2CH_3 \rightarrow C_2H_6 \quad [33]$$

$$2CH_2{:}CH\cdot\dot{C}H_2 \rightarrow \text{1,5-hexadiene} \quad [34]$$

$$CH_3 + CH_2{:}CH\cdot\dot{C}H\cdot CH_3 \rightarrow \text{pentene} \quad [35]$$

$$CH_2{:}CH\cdot CH_2 + CH_2{:}CH\cdot\dot{C}H\cdot CH_3 \rightarrow \text{heptadiene} \quad [36]$$

$$CH_2{:}CH\cdot\dot{C}H_2 + H \rightarrow \text{propylene} \quad [37]$$

$$H + H + M \rightarrow H_2 + M. \quad [22]$$

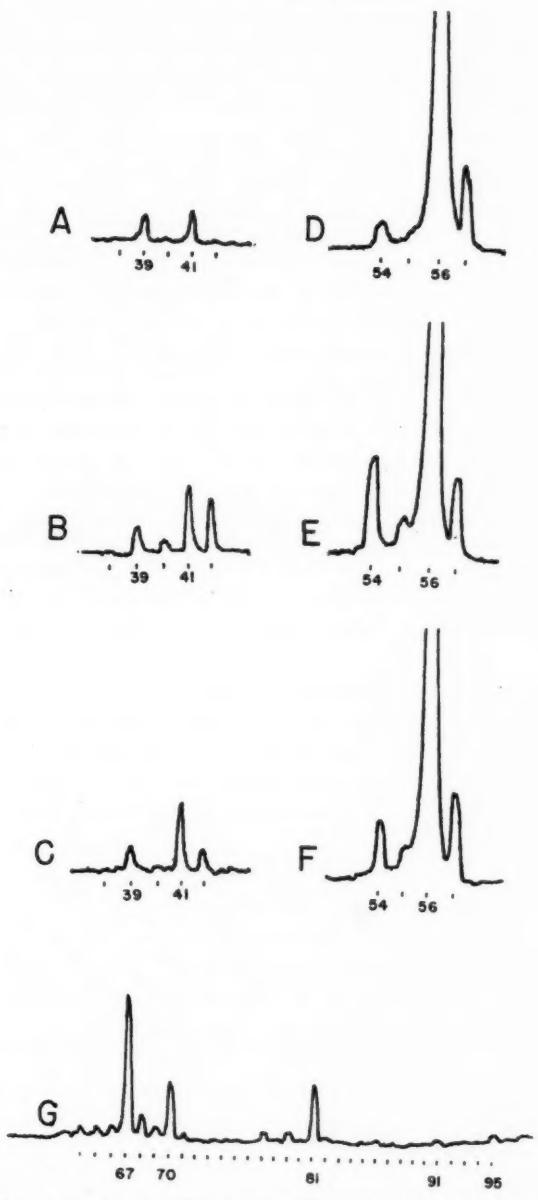

FIG. 3. Portions of mass spectra illustrating the detection of allyl and methallyl radicals in the decomposition of 1-butene. As described in the section on 1-butene, the propylene and butadiene are formed as secondary products.

It is interesting to compare the energies required for the two primary steps given above. From ΔH_f(allyl) = 32 kcal./mole (22), $\Delta H_f(CH_3)$ = 32.6 kcal./mole (13), ΔH_f(γ-methallyl) = 26 kcal./mole (22), ΔH_f(1-butene) = 0.280 kcal./mole (25), and ΔH_f(H) = 51.5 kcal./mole, the following bond dissociation energies can be derived:

$$D(\text{allyl–}CH_3) = 64 \text{ kcal./mole},$$

$$D(\text{methallyl–H}) = 77 \text{ kcal./mole}.$$

If the decomposition of 1-butene proceeds, as seems probable, by the formation of an excited molecule (26), then this molecule would suffer bond rupture after the time interval required for sufficient vibrational energy to become associated with a particular bond. Although the C–H bond is stronger than the C–C, the difference is only about 13 kcal., and it is not surprising that a molecule with 112 kcal. of excitation energy should be able to decompose by either mode. It is not possible from the present data to establish the relative probabilities of reactions [29] and [30], but the greater abundance of the ethane and hexadiene over the pentene and heptadiene, as well as the relative size of the radical peaks, indicates that the C–C split predominates. The low yield of H_2 compared with that found for propylene and 2-butene is also consistent with a smaller probability for the C–H split. The proportion of H_2 found is not much greater than was estimated above to result from the reaction of excited mercury atoms with the allyl radicals from propylene.

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RADIOIODINE EXCHANGE BETWEEN IODOSTEARIC ACID MONOLAYERS AND SUBSTRATE IODIDE[1]

By R. F. Robertson, C. A. Winkler, and S. G. Mason

ABSTRACT

Velocities of exchange of iodine between monolayers at the air/water interface of α-iodostearic acid and potassium iodide in the substrate have been measured over a range of monolayer and substrate concentrations and temperatures using a radioactive tracer technique. The pressure–area isotherms were also determined. The process was followed by measuring the decrease in counting rate immediately above the surface. It is shown theoretically that ions released to the substrate diffuse rapidly and do not contribute appreciably to the counting rate. The velocity of exchange was found to be first order in concentration of the surface phase and of higher but indeterminate order in concentration of potassium iodide. In the region of 18°C., where a transition from liquid-condensed to liquid-expanded film occurs, the reaction velocity constant undergoes a discontinuous increase. Activation energies of 8.0 and 10.8 kcal./mole were found for exchange in the condensed and expanded films respectively.

INTRODUCTION

The kinetics of chemical reactions occurring in monolayers at air/water interfaces have been studied by following changes in the surface potential (22), or in the area per molecule at constant pressure in the film (5). The reactions studied thus far have been limited to oxidation (4, 18, 22, 26), hydrolysis (5, 3, 16, 6, 27, 13, 28), and lactonization processes (12, 24). Both experimental methods involve indirect measurement of the changes in concentration of the reactants in the surface films from which the reaction velocity is computed. A more direct method of following such reactions is to use monolayers containing radioactively tagged groups which on reaction pass into the substrate. Such a method could also be used to study exchange reactions between films and substrates.

Tracer techniques have already been used in the study of soluble films (14). Carbon-14 tagged films deposited by the method of Blodgett (9) on various surfaces have been used to measure backscattering and chemical reactions in adsorbed films (7), to investigate lubrication problems (10), and to study surface diffusion phenomena (15). Deposited radioactive monolayers have been proposed as standard β-ray sources because of their stability and ease of reproduction and negligible self-absorption (8).

To the present, however, no investigations of insoluble monolayers at the air/water interfaces have been reported in which the tracer technique has been employed. In this paper a successful application of the method to the study of halogen exchange between a tagged monolayer molecule and a reactant in the substrate is described. Results are presented for iodine-exchange between monolayers of α-iodostearic acid and potassium iodide substrates at various surface and substrate concentrations over a range of temperatures.

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Contribution from the Department of Chemistry, McGill University, Montreal, Que. Based on work conducted under Extra-Mural Grant 2031-08 of the Defence Research Board of Canada.

EXPERIMENTAL PART

Materials

Radioiodine was incorporated by an exchange reaction into α-iodostearic acid which was prepared from the corresponding bromo acid. Iodine-131 was selected as the tracer element because it is a β-emitter of intermediate energy (0.6 Mev.), has a convenient half life (8.0 days), and is readily available in carrier-free form.

α-Bromostearic Acid

This acid, prepared from purified stearic acid by the method of Hell and Sadomsky (21), was recrystallized 10 times from petroleum ether (40°–60°C. boiling range) and three additional times from 95% ethanol at −13°C. The pure α-bromostearic acid crystallized as white needles and plates. Melting point 60.1–60.5°C. (Hell and Sadomsky 60°C.).

α-Iodostearic Acid

This acid was prepared essentially by the method of Frewing (17). α-Bromostearic acid (0.058 mole) was refluxed with KI (0.116 mole) in 300 ml. of 95% ethanol for three hours. The ethanol was then removed *in vacuo* and the α-iodostearic acid dissolved in hot benzene. After eight recrystallizations at +8°C. from benzene, the acid was recrystallized three additional times from 95% ethanol at −13°C. The crystals were similar in appearance to those of the α-bromostearic acid. Melting point 67.0–67.3°C. (Frewing 67°C.).

Radioactively Tagged α-Iodostearic Acid

The exchange was carried out in a 250 ml. erlenmeyer flask with a rounded bottom. One ground-glass joint was attached to the neck of the flask, and a second to the side just above the rounded bottom.

Ten millicuries of aqueous carrier-free and buffered NaI^{131} solution (AECL grade) was placed in the flask and the water removed by freeze-drying. A weighed sample of 0.01 to 0.02 gm. of inactive α-iodostearic acid was dissolved in 4 ml. of 95% ethanol and added to the reaction flask over the freeze-dried residue (largely buffer). The resulting solution was gently refluxed for two to three hours to allow the exchange reaction to occur, and then allowed to cool to room temperature.

A sintered-glass filter tube was inserted in place of the stopper in the ground-glass joint on the side, the flask was tipped until the filter was elevated somewhat above the body of the flask, and 200 ml. of 1 *N* HCl solution was added. An emulsion of fatty acid in HCl solution formed initially, but after the flask had been left for two to three hours or sometimes overnight, fairly large aggregates of fatty acid appeared. The aqueous layer was then filtered off, the fatty acid being retained on the flask walls and on the filter. Two consecutive 50 ml. portions of 0.1 *N* HCl were then added to the flask and the precipitate of fatty acid washed as completely as possible on to the filter where it was again washed twice with 25 ml. portions of distilled water. The flask was again connected to the freeze-drying apparatus and the water completely removed from the flask and filter tube.

The dry I^{131} α-iodostearic acid on the sides of the flask and on the filter was dissolved by washing with warm benzene. The resulting solution was then made up to volume with benzene in a 25 ml. volumetric flask. The benzene solution of I^{131} α-iodostearic acid was stored in the stoppered volumetric flask away from light, behind a lead shield. The concentration of α-iodostearic acid in the benzene solution was determined, when necessary, from the measured pressure–area relation of a known volume of the fatty acid solution, spread to form a monolayer.

The relative quantities of NaI^{131} and α-iodostearic acid used in the above preparations were chosen by calculation to give an experimentally convenient initial radioactive counting rate of about 5000 counts per cm.^{2} per min. when the acid is spread on a surface area of about 40 Å^2 per molecule. In the calculation it was assumed that 50% exchange represented complete reaction and that the over-all counting efficiency was 50%. The counting rates found experimentally were surprisingly close to the expected values.

Other Materials

All the materials used in the experiments and preparations, including the paraffin used in coating the monolayer trough, were purified to ensure the absence of surface-active contaminants. Routine checks were made by spreading pressure measurements in the conventional way.

Apparatus

The general arrangement of the monolayer trough and accessory equipment is shown in Fig. 1. The stainless steel trough (carefully coated with paraffin

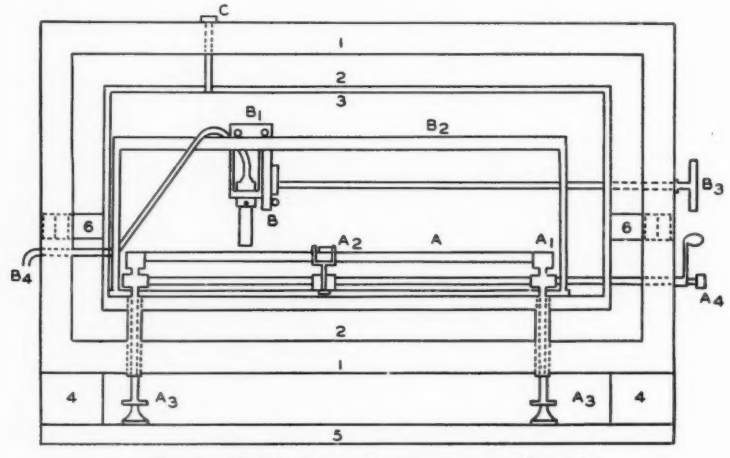

FIG. 1. Monolayer trough arrangement (schematic).

Air bath: 1, insulation; 2, chamber containing copper coils; 3, air chamber; 4, cork supports; 5, stone pedestal; 6, windows (triple glass).

Film trough: A, trough; A_1, trough support; A_2, barrier moving device; A_3, adjustable feet; A_4, barrier moving device.

Geiger tube assembly: B, Geiger tube; B_1, tube carriage; B_2, tracks for carriage; B_3, handle tube carriage; B_4, shielded lead to rate meter.

Surface balance: C, sleeve for wire of surface balance.

before use) was enclosed in an air bath, the temperature of which was held constant by pumping water from external thermostats (not shown) through copper coils in the air bath. The water in the trough was also held to constant temperature by circulation of water from the thermostats. The temperature of the solution in the trough could be controlled manually to within ±0.2°C. of the temperature of the air bath. A reservoir of water, into which filter paper hung and which was similarly held at constant temperature, maintained a saturated atmosphere within the air bath. After temperature equilibration the temperature of the air bath could be held within ±0.1°C. for periods of 15 hr. in the range of 10°C. to 40°C.

The surface balance was the Harkins vertical pull type (20). An image of a hairline was reflected from a small mirror mounted at the main knife edge of the balance, and projected on a curved scale. The balance had a sensitivity of 0.48 dyne per cm. per scale division of the optical lever.

The barrier of the trough could be operated by remote control from outside the box and its position in the trough could be determined from the reading on an externally mounted revolution counter. The Geiger tube mounting was also remote-control-operated from outside the box. The Geiger tube, which had an effective window area of 2 cm.^{2}, could be moved to scan any region of the film surface when the tube was fixed in its carrier.

The counting equipment consisted of an Electronics Associates type 1725 Ratemeter used in conjunction with an Esterline-Angus 10 milliamp. recording milliammeter. The counting rate could be recorded as a function of time on the chart of the milliammeter. The Geiger tube was a mica end-window counter (Nuclear Instrument Corp. type D 34). The fused mica/glass seal eliminated tube failures experienced with cemented mica-end-window tubes in the saturated atmosphere.

Experimental Procedure

All substrates used in the present work were allowed to come to constant temperature overnight. The technique used to obtain the pressure–area isotherms was essentially that of Adam (2). The substrate was 0.01 *N* HCl solution. Before the film was spread the surface was repeatedly swept by the barriers until a decrease in area to one-third of the original caused less than 0.05 dyne/cm. increase in surface pressure.

To spread a film, a measured volume of benzene solution of α-iodostearic acid was added dropwise at many points on the surface from an Agla micrometer syringe. Fifteen minutes were allowed for the evaporation of the benzene, the initial pressure was noted, and the film was compressed in steps every three to four minutes. Since the surface balance did not permit accurate measurements of decreases in surface pressure, only compression curves were obtained.

The same spreading technique was used in the exchange experiments except that the Agla syringe was replaced with a microliter syringe-pipette. Sufficient acid was added to the surface during spreading to bring the surface pressure to a value just below that desired for the exchange experiment. The final pressure adjustment was made by compression of the film.

The slide of the surface balance was removed after each pressure measurement during an exchange reaction to prevent undue contamination with substrate solution and film molecules, and was cleaned between each measurement. At the end of an exchange experiment the active film was removed by suction through a capillary pipette to a suction flask.

Directly after the trough was filled with KI solution the Geiger tube was mounted in position with the end window 3 mm. above the surface to allow passage of the barrier and left inside the air bath during the period of thermal equilibration. The background counts were about 60 per min.; since the counting rates obtained with the films were of the order of 10^4 per min., no correction for background was necessary.

Standard radiochemical techniques and precautions were used at all stages of preparation and use of the radioactive fatty acid.

RESULTS

Pressure–Area Isotherms

To characterize the various types of monolayer, pressure–area isotherms were determined over 0.01 *N* HCl substrates. Because of rapid contamination

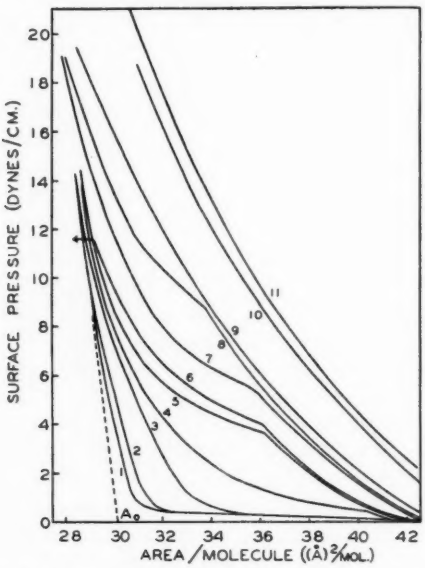

FIG. 2. Pressure–area isotherms of α-iodostearic acid.

Curve	Temp.	Curve	Temp.	Curve	Temp.
1	9°C.	5	16.4°C.	9	19.8°C.
2	10.6°C.	6	16.8°C.	10	26.4°C.
3	12.6°C.	7	17.4°C.	11	27.4°C.
4	14.8°C.	8	18.8°C.		

A_0 = area at zero compression = 30.2 Å²/molecule.

of the slide of the surface balance when salts were present in the substrate solution, it was not possible to measure the isotherms over substrates containing potassium iodide at the relatively high concentrations used in the monolayer/substrate exchange experiments.

The isotherms between 9° and 27.4°C. are presented in Fig. 2 and are typical of fatty acids. The curves indicate the existence of three distinct types of film which may be illustrated by reference to the 17.4°C. isotherm:

1. From very low pressures up to a pressure 5.5 dynes/cm. and an area 38.95 Å²/molecule, the film is "liquid-expanded" in the nomenclature of Adam (2). The coefficient of compressibility $K = 1/A\ (\partial A/\partial \pi)$, where π is the surface pressure and A is the area per molecule, is 2.9×10^{-2} cm./dyne, which may be compared with values of 2×10^{-2} to 7×10^{-2} cm./dyne given by Harkins (19) for this type of film.

2. Above the pressure 5.5 dynes/cm. the film is "intermediate-liquid", the initial K being 1.1×10^{-1} cm./dyne.

3. As the pressure is further increased the isotherm shows a gradual transition to a "liquid-condensed" film. At 28.45 Å²/molecule, $K = 9\times10^{-3}$ cm./dyne.

Above 19.8°C. the films are of the liquid-expanded type. Below this temperature an intermediate-liquid film exists down to about 12°C. Between 12°C. and 19.8°C., the films are liquid-expanded at low pressures up to a transition pressure, which increases with increasing temperature, when condensation to an intermediate-liquid film occurs. As the pressure is increased the intermediate-liquid film passes gradually to the liquid-condensed film.

The isotherms yield an area at zero compression of about 30.2 Å²/molecule. This value lies between 27.8 Å²/molecule and 32.8 Å²/molecule for the C_{16}–C_{17} and C_{18}–C_{21} α-bromo acids respectively (1). The marked tendency to collapse exhibited by α-iodostearic acid monolayers at temperatures below 12°C. as the surface pressure was increased above about 10 dynes/cm. made it impossible to determine the pressure–area isotherms over a large range of pressures in this condensed state. The area at zero compression may consequently be in error by as much as +1 Å²/molecule.

Preliminary Exchange Experiments

When a monolayer of the tagged acid was deposited on a substrate containing 0.01 N HCl and potassium iodide, the counting rate decreased with time. A series of preliminary experiments showed that the rate of the process, as measured by the rate of change of counting rate, increased with increased KI concentration. From these experiments it was concluded that 1.0 M KI was the most convenient concentration for temperature coefficient measurements. Measurements at concentrations in excess of 1.5 M KI were found impractical because of crystallization of the salt on the barriers.

In the experiments, condensation of water on the end window of the Geiger tube could conceivably occur and thus cause an apparent decrease in counting rate. It was shown however that this had a negligible effect on the counting rate. In further experiments it was shown that when the film was swept off

at any time the counting rate dropped to the normal background value of about 60 per min. so that the activity transferred from the monolayer to the substrate has a negligible influence on the background count.

The possibility that the decrease in counting rate was due to hydrolysis of the α-halogen compound to the corresponding α-hydroxy compound was investigated in a series of experiments using active films spread on 0.01 *N* HCl, and 0.01 *N* HCl substrates containing 1.0 *M* and 2.0 *M* KCl. In no case did any significant decrease in counting rate with time occur. Some films spread on 0.01 *N* NaOH substrates to favor hydrolysis also showed no decrease in counting rate with time.

All the foregoing experiments were made at constant total area; in all instances, including those over the KI substrates, the surface pressure remained constant, which indicated a constant chemical composition of the film. These experiments also left little doubt that the decrease in counting rate of the film on a KI substrate was associated with the presence of I^- ion in the substrate and that the observed decrease in counting rate was due to iodine exchange between the alkyl halide in the monolayer and inorganic iodide in the substrate.

Exchange Reaction

The rate of the exchange reaction was studied at various values of the surface pressure, temperature, and concentration of potassium iodide in the 0.01 *N* HCl substrate. The rate was computed in the following manner:

Let V moles cm.$^{-2}$ min.$^{-1}$ be the velocity (forward and reverse) of the exchange reaction

$$CH_3(CH_2)_{15}CHI^*COOH + KI \rightarrow CH_3(CH_2)_{15}CHICOOH + KI^*.$$

Let n moles/cm.^{2} be the total concentration of fatty acid in the film, and $f(t)$ be the fraction of fatty acid molecules containing radioactive atoms at time t. Assuming that the radioactive atoms are homogeneously distributed in the surface film, the rate of disappearance of radioactive atoms from the surface film is $V f(t)$, i.e.

$$-d(nf(t))/dt = Vf(t), \quad [1]$$

which, on integration, yields

$$\log_e[f(0)/f(t)] = Vt/n. \quad [2]$$

If it is further assumed that the recorded counting rate $c(t)$ is proportional to $f(t)$, i.e radioactive atoms passing into the substrate do not register on the counter, Eq. [2] becomes

$$\log_e[c(0)/c(t)] = kt, \quad [3]$$

where $k = V/n$.

Semilogarithmic plots of $c(t)$ against t in most cases yielded straight lines from which the rate constant k could be readily determined. Typical examples are illustrated in Fig. 3 for films at 25°C. and 35°C. Exceptions occurred at 18°C. as shown in Fig. 4, where the plot became linear only after approximately two hours of exchange.

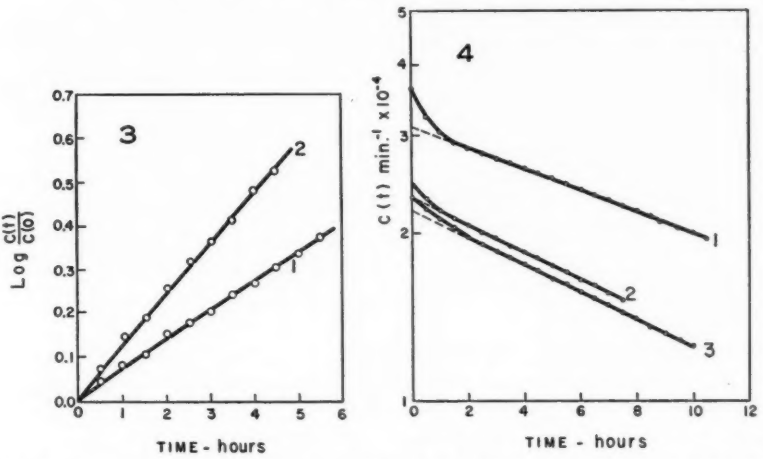

FIG. 3. Counting rate vs. time plots at 25°C., 15.5 dynes/cm. (curve 1) and 35°C., 14.6 dynes/cm. (curve 2).
FIG. 4. Semilogarithmic plots of counting rate vs. time at 18°C. at surface pressures of 14.8 dynes/cm. (curve 1) 4.3 dynes/cm. (curve 2), and 3.9 dynes/cm. (curve 3).

Values of k at various temperatures between 10°C. and 37°C. and at various surface pressures over 1.0 M KI+0.01 N HCl substrates are summarized in Table I. It will be noted from Table I that at a given temperature k is independent of surface pressure and hence surface concentration. This is also approximately true for the linear portion of the 18°C. plots.

TABLE I

SUMMARY OF RATE CONSTANTS
Substrate: 1.0 M KI+0.01 N HCl

Temperature, °C.	Surface pressure, dynes/cm.	Approximate surface concentration, molecules/cm.² ×10¹⁶	Probable film type†	$k\times10^4$, min.⁻¹
10	4.2	3.3	Lc	5.80
	7.8	3.4	Lc	5.80
14	4.2	3.13	Lc	6.85
	12.9	3.47	Lc	7.00
18	3.9	2.68		9.30
	4.3	2.69		9.20
	14.8	3.38		7.70
22.5	7.0	2.78	Le	20.9
25	2.1	2.39	Le	25.3
	15.5	3.09		24.7
35	14.6	—	Le	43.3
	16.8	—	Le	44.9
37	9.9	—	Le	51.1

*Estimated from π–A plots (Fig. 2) on KI-free substrates.
†Lc = *liquid condensed*; Le = *liquid expanded.*

The Arrhenius plot for the temperature coefficient of k is given in Fig. 5 and shows two linear portions separated by a discontinuity between 14°C. and 22.5°C. The calculated activation energies are 10.8 kcal./mole in the higher and 8 kcal./mole in the lower temperature range.

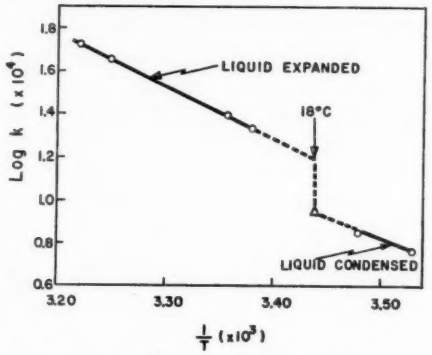

FIG. 5. Arrhenius plot of k for 1.0 M KI+0.01 N HCl substrates.

The variation of k with concentration of KI in the substrate was measured at a surface pressure of 7.7 dynes/cm. and at a temperature of 22.5°C. The experimental values are given in Table II. The rate constant k increases rapidly

TABLE II

INFLUENCE ON k OF KI CONCENTRATION IN 0.01 N HCl SUBSTRATES

Temperature = 22.5°C., surface pressure = 7 dynes/cm.

Concentration KI, moles/liter	$k \times 10^4$, min.$^{-1}$
0.25	4.60
0.5	5.90
1.0	20.9
1.5	24.9

with increase in KI concentration, particularly between 0.5 and 1.0 M, but the order of the reaction in concentration of KI could not be determined.

DISCUSSION

In computing the exchange velocity it is not strictly correct to assume, as above, that the counter detects the radioactive atoms in the surface film but not in the substrate. Time is required for the I^- ions released from the surface to diffuse to a distance beyond which, because of β-particle absorption by the water, they make a negligible contribution to the counting rate. However, if the rate of exchange is much less than the rate of diffusion of I^- ions into the substrate, the method of calculation is acceptable. That this condition prevails can be demonstrated by the following argument.

If it is assumed that the exchange occurs instantaneously, it is possible to

calculate the decrease with time of the radioactive counting rate that results from diffusion of the radioactive ions away from the surface. The basic equation for diffusion in the substrate may be written

$$\partial C/\partial t = D\partial^2 C/\partial x^2, \quad [4]$$

where C is the volume concentration of radioactive ions at time t at a distance x below the surface, and D is the self-diffusion coefficient of the ions.

If at time $t = 0$, $C = 0$ for all values of x', the solution of Eq. [4] corresponds to that of a one-dimensional diffusion in a semi-infinite system having an instantaneous plane source at $x = 0$ and is given by (23)

$$C = (s/\sqrt{\pi Dt}) \cdot e^{-x^2/4Dt}, \quad [5]$$

where s is the amount of radioactive iodine instantaneously released per unit area of surface.

For simplicity an exponential absorption may be assumed for the β-radiation passing through the substrate to the counter. Then the contribution to the counting rate due to a layer of thickness dx at x is

$$dc(t) = \alpha C \cdot e^{-\mu x} dx, \quad [6]$$

where μ is the absorption coefficient of the substrate and α is a proportionality constant related to counter efficiency and the disintegration constant of the radioactive species.

Combining Eqs. [5] and [6] and integrating yields the total counting rate of the diffusing ions as

$$c(t) = \frac{s}{\sqrt{\pi Dt}} \int_0^\infty \exp\left[-\left(\frac{x^2}{4Dt} + \mu x\right)\right] dx, \quad [7]$$

for which the solution is readily shown to be the remarkably simple relation

$$c(t) = c(0) \cdot e^{-D\mu^2 t}. \quad [8]$$

Eq. [8] is identical with Eq. [3] when $k = D\mu^2$. Taking $D = 1.7 \times 10^{-5}$ cm.^{2}/sec., which is the mean experimental value for I^- in NaI (31), and $\mu = 26.6$ cm.$^{-1}$, which is assumed identical with that of aluminum for the β-radiation of iodine-131 (32), $k = D\mu^2 = 7200 \times 10^{-4}$ min.$^{-1}$. This is several orders of magnitude greater than the values given in Tables I and II. Furthermore D, and therefore $D\mu^2$, is for all practical purposes constant, whereas the experimental values of k increase rapidly with increase in I^- concentration.

It may therefore be safely concluded that exchange rather than diffusion is the rate-controlling step in the process measured.

The values of k $(= V/n)$ in Table I appear to be independent of surface pressure, and hence surface concentration, over the range studied at the indicated temperatures. The exchange reaction is therefore first order in concentration of monolayer molecules.

As noted previously the Arrhenius plot was discontinuous between 14°C. and 22.5°C. (Fig. 5) and the exchange reaction at 18°C. failed to show first

order behavior over the initial one and one-half to two hours of exchange (Fig. 4). The "critical temperature" for the disappearance of the intermediate-liquid film occurred near this temperature (Fig. 2). The failure of the 18°C. experiments to show the same first order behavior as shown at other temperatures might arise from the simultaneous presence of condensed and expanded liquid films under non-equilibrium conditions on the surface. The over-all exchange velocity would then result from two simultaneous reactions with different rates and associated with the two types of film present.

The discontinuous increase in reaction velocity and activation energy near 18°C. is probably a direct result of the change in surface phase from liquid-condensed to liquid-expanded which occurs in the region of 18°C. Similar discontinuities have been observed by Rideal and others (5, 12, 16, 26) in hydrolysis and oxidation studies in monolayers. The differences in the activation energies were considered by Rideal to arise from changes in the configuration and orientation of monolayer molecules in the surface and hence were attributed to a change in the steric factor of the collision theory treatment of reaction kinetics. The same might apply to the present systems.

Activation energies for homogeneous isotopic halogen exchange in bulk of halogenated acids similar to α-iodostearic acid have been determined. Values of 16 kcal./mole for free α-iodoacetic acid and 17 kcal./mole for the methyl ester have been reported for isotopic iodine exchange with I^- in aqueous solution (29). The value of the activation energy of isotopic bromine exchange between Br^- and α-bromopropionic acid in H_2SO_4 was found to be 20.9 kcal./mole (25). The value of 10.8 kcal./mole found in the present exchange for the expanded film is thus between 5 and 6 kcal./mole lower than the activation energy for similar iodine exchanges in solution. This decrease in activation energy may be associated with a small steric factor for the monolayer exchange in terms of collision theory treatment. In other kinetic studies of monolayer reactions the steric or accessibility factor was found to be essentially unity for reactions involving the α position (22).

Aliphatic halogen exchange reactions are considered to proceed through the mechanism of the Walden inversion (11, 30). The entering halogen ion has been shown to have the greatest probability of substitution if it approaches the carbon atom holding the exchangeable atom from a direction normal to the face of the carbon tetrahedron opposite the atom to be replaced. In monolayers the poor accessibility of this tetrahedron face to the I^- ions might be the cause of the apparent low steric factor in the exchange kinetics, and the change of activation energy observed might be the result of a change in accessibility in going from the condensed to the expanded liquid film.

To obtain the specific rate constant k_s for the exchange reaction the true order of the reaction in monolayer concentration and substrate I^- concentration must be known. Since the reaction is first order in monolayer concentration, the relationship between the over-all velocity and the specific rate constant is given by

$$V = k_s n m^y,$$

where m is the concentration of I^- in the substrate and y the order of the reaction with respect to I^-.

To obtain k_s, the value of y must be determined. In the present investigation it was not possible to determine the true order of dependence on KI concentration. The values of k in Table II do not fit any simple order when the concentration of the substrate solution is used as the effective surface phase concentration. The apparently anomalous dependence of reaction velocity on KI concentration might be resolved if it were possible to calculate the change in concentration in the solution as the monolayer is approached. At present no method exists for calculating the concentration of I^- at the surface; this concentration will depend, among other factors, upon the structure of the electrical double layer existing at the interface.

The behavior of the film itself as the substrate KI concentration is increased must not be overlooked as a possible cause of the anomalous concentration dependence of the exchange. No pressure–area curves could be obtained on KI substrates, and it was assumed that the film characteristics were not greatly changed with increasing KI concentration. This requires experimental confirmation.

While the experimental findings of this investigation are of a preliminary nature and must be extended before further conclusions regarding the detailed mechanism of exchange can be drawn, it is nevertheless considered that these results demonstrate the value of the radioactive tracer method in monolayer systems.

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THE SURFACE ENERGIES OF CALCIUM OXIDE AND CALCIUM HYDROXIDE[1]

By Stephen Brunauer, D. L. Kantro, and C. H. Weise

ABSTRACT

The total surface energies (or surface enthalpies) of calcium oxide and calcium hydroxide were determined by measuring the heats of solution in 2 *N* nitric acid of calcium oxide and calcium hydroxide having high and low specific surface areas, and by determining the surface areas by the B.E.T. method, using nitrogen as adsorbate. The molecular area of nitrogen was taken to be 16.2 $Å^2$ at 77.3°K. Precision determinations of the lattice parameters indicated that the high and low surface substances had the same unit cell dimensions, and X-ray line broadening measurements indicated that the crystals were perfect or nearly perfect. The surface energy of calcium oxide at 23°C. was found to be 1310 ± 200 erg/cm.^{2}, which compares well with the theoretical value of 1100 erg/cm.^{2} The surface energy of calcium hydroxide at 23°C. was found to be 1180 ± 100 erg/cm.^{2} The heat of the reaction CaO (*c*, 23°) $+ H_2O$ (*l*, 23°) $= Ca(OH)_2$ (*c*, 23°), for crystals having negligible specific surface areas, was found to be $-15{,}620$ cal.

INTRODUCTION

In 1927 and 1928, Lipsett, Johnson, and Maass (18) published three papers on the surface energy of sodium chloride. They determined the heats of solution of coarsely crystalline and finely divided sodium chloride, measured the surface area microscopically, and obtained the surface energy from the ratio of the energy difference to the difference in surface area. The quantity thus measured is really the surface heat content or enthalpy; however, since Gibbs, it has been customary not to make a distinction between surface enthalpy and total surface energy (or, briefly, surface energy). The investigators concluded, "... the surface energy of sodium chloride is found to be about 400 ergs per sq. cm. The errors involved in these measurements are of necessity rather large, and this figure can be regarded as only approximate. It will serve to show, however, the practical applicability of this method to the determination of the surface energy of solids, for which experimental data, so far, are sadly lacking."

The largest error in the above work was in the determination of the surface area of sodium chloride. Only the geometrical surface is visible in the microscope; surface roughnesses of a molecular scale are not visible even in an electron microscope. If the "roughness factor" of the sodium chloride was, let us say, 1.33, the surface area was 33% larger than that measured with the microscope, and the surface energy was only 300 erg/cm.^{2}

Twenty-seven years have passed since 1928, and experimental data on the surface energies of solids are still "sadly lacking". Meanwhile, reliable methods of surface area determination were developed and widely used, yet the problem of the surface energy of sodium chloride is not fully solved to date. The most recent information on the subject is found in a paper of Benson and Benson (1), who prepared sodium chloride samples of widely differing surface areas and determined the surface areas by the B.E.T. method (3), using

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Contribution from the Portland Cement Association Research and Development Laboratories, Chicago, Illinois.

nitrogen as the adsorbate. Because of slight quantities of impurities, the effects of which on the surface energy the authors were unable to estimate, they regarded their surface energy value of 305 erg/cm.^{2} as "provisional". If the effects of impurities on the heats of solution were additive, the value of Benson and Benson must be close to the true surface energy of sodium chloride.

The only other reliable experimental surface energy value published so far is that of Jura and Garland (14) for magnesium oxide. In this case, also, the authors pointed out that their surface energy value may have been in error; and in the light of the results reported in this paper, their value for magnesium oxide does appear to be somewhat too low.

Theoretical evaluations of the surface energies of certain ionic crystals, crystallizing in cubic lattices, were made by a number of investigators, but these are only rough approximations. The scarcity of data on surface energies is so much the more surprising, since the interest in surface chemistry in general, and in adsorption in particular, has tremendously increased in the last decade and a half. Energy changes occurring in adsorption were widely investigated, but the investigators usually interpreted the changes as being due to a change in state of the adsorbate and assumed, for convenience, that the change in state of the surface of the adsorbent was negligible. The theoretical arguments advanced in favor of this assumption were inadequate, and experimental data were wholly lacking. It seems that a systematic investigation of the energy contents of a variety of surfaces could throw some light on this problem. It could, probably, also furnish some useful information as to the validities of various theories advanced for the structures of solid surfaces, such as, for example, the theory developed by Weyl (30).

In the present investigations, the surface energies of calcium oxide and calcium hydroxide were obtained by determining the heats of solution in 2 *N* nitric acid of samples having different surface areas, and measuring the surface areas by the B.E.T. method (3), using nitrogen as the adsorbate.

EXPERIMENTAL

Calcium Oxide

The low surface calcium oxide, Batch A-40, was prepared from Fisher's certified reagent grade calcium carbonate. The calcium carbonate was ignited at 1050°C. for four hours, cooled, and pressed into pellets, $\frac{1}{4}$ in. in diameter and $\frac{1}{4}$ in. to $\frac{3}{8}$ in. long, by a Parr pellet press. The pellets were then ignited at 1300°C. for 64 hr., and cooled and stored in a desiccator containing phosphorus pentoxide. Prior to use, each sample was ignited at 1050°C. for 30 min., cooled in a phosphorus pentoxide desiccator, weighed, and then introduced immediately into the calorimeter or the adsorption apparatus.

The high surface calcium oxide, Batch A-39, was prepared from calcium hydroxide, Batch E-4. Each sample was separately prepared before use. The calcium hydroxide was ignited at 1050°C. for 30 min., cooled for 15 min. over fresh phosphorus pentoxide in a desiccator, weighed, reignited at 1050°C. for 15 min., again cooled for 15 min., then immediately introduced into the calorimeter or the adsorption apparatus. The samples were not weighed after

the second ignition. The first ignition always gave the correct ignition loss, and it was assumed that the weight after the second ignition was the same as after the first ignition. A single ignition, with subsequent weighing, gave far less reproducible results.

In handling both calcium oxide and calcium hydroxide, extreme precautions were taken to avoid contamination of the materials by atmospheric moisture and carbon dioxide. To the extent possible, all operations, including pelleting, were carried out in a controlled-atmosphere cabinet.

All samples of calcium oxide and calcium hydroxide were exposed to the atmosphere only while they were being dropped into the calorimeter, which period never exceeded five seconds. To ascertain the amount of moisture picked up in this short time, the following experiment was performed. (1) A 1 gm. sample of calcium oxide, A-39, was prepared as described above. (2) After the final cooling period, the covered platinum crucible with the sample was transferred from the desiccator into a weighing bottle inside the controlled-atmosphere cabinet. (3) The weighing bottle, with its contents, was weighed. (4) The sample was exposed to the atmosphere over the calorimeter bath for five seconds. The crucible was then covered, returned to the weighing bottle, the weighing bottle was covered, and the weight was determined. (5) The procedure of step (4) was repeated three times, except that each exposure interval was 20 sec.

The experiment was performed on three separately prepared samples, with the result that the amount of moisture picked up in five seconds was *at most* 0.13 mgm./gm. Actually, no gain in weight occurred in the first five seconds, probably because time was needed for the moisture to reach the sample after the opening of the crucible. It is possible that a shorter time delay would have occurred if the sample had been dropped into the calorimeter funnel. The moisture gain was very close to linear with time between 5 sec. and 45 sec., with a slope of 0.13 mgm./gm. per 5 sec.

Calcium Hydroxide

The coarsely crystalline calcium hydroxide, Batch E-4, was prepared in a manner similar to that employed at the National Bureau of Standards (20). A 100 ml. beaker, filled with saturated sodium hydroxide solution, and a 150 ml. beaker, filled with saturated calcium nitrate solution, were placed in a large jar. Both chemicals were Baker's analyzed reagent grade, and deionized water was used. Water was then added to the jar until the liquid level was about one inch above the level of the taller beaker. Care was taken to avoid mixing. The jar was covered, and was left standing undisturbed for about two weeks, by which time a growth of calcium hydroxide crystals practically filled the mouth of the beaker containing the calcium nitrate solution. The calcium hydroxide crystals were removed from the beaker in the controlled-atmosphere cabinet, washed several times with water, and dried overnight at a water vapor pressure of 0.5 μ of mercury. The dry calcium hydroxide was sieved in the cabinet; the fraction passing a U.S. Standard No. 30 sieve was discarded, and the rest was stored in paraffin-sealed weighing bottles until used.

The high surface calcium hydroxide, Batch E-8, was prepared by vapor phase hydration of calcium oxide in a manner similar to that described by Thorvaldson and Brown (26). Fisher's certified reagent grade calcium carbonate was ignited at 1050°C. for four hours, cooled in a desiccator containing phosphorus pentoxide, and crushed in the controlled-atmosphere cabinet to pass a U.S. Standard No. 100 sieve. The calcium oxide was then distributed among several tared polyethylene weighing bottles, which were placed over water in a desiccator jar. The bottles were weighed periodically. When the water content had risen to a value 35% in excess of the stoichiometric quantity, the material was removed and dried at a water vapor pressure of 0.5 μ of mercury. The dry calcium hydroxide was pressed into pellets, $\frac{1}{4}$ in. in diameter and $\frac{1}{4}$ in. to $\frac{3}{8}$ in. long, in a Parr pellet press inside the controlled-atmosphere cabinet, and the pellets were stored in paraffin-sealed weighing bottles until used.

After vacuum drying and pelleting, Batch E-8 contained 0.76% excess water. This corresponded approximately to a quantity of water sufficient to cover the entire surface of the calcium hydroxide with an adsorbed monolayer of water. To obtain a sample with less excess water, half of Batch E-8 was heated at 180° to 200°C. for 16 hr. in a vacuum of the order of 10^{-6} mm. of mercury. The batch, E-8A, contained only 0.12% excess water, but the heating resulted in some sintering. The pellets were stored in paraffin-sealed weighing bottles until used.

An experiment similar to that performed on calcium oxide, and described in the previous section, was made on calcium hydroxide, Batch E-8A, to ascertain the water pickup during the five seconds of introduction of the sample into the calorimeter. The amount of water picked up was less than 0.1 mgm./gm.

X-Ray Measurements

X-Ray powder diffraction patterns were obtained by means of a North American Philips wide range Geiger counter diffractometer. The basic unit was operated at 40 kv. and 20 ma. Copper K_α radiation was used; the K_β component was removed by a nickel filter. For precision determinations of the lattice parameters, the goniometer scanning rate was $\frac{1}{4}$°/min. and the chart speed was 1 in./min., so that readings could be made to the nearest 0.02°2θ.

For each calcium oxide sample six lines and for each calcium hydroxide sample seven lines were recorded in the back-reflection region. Relative intensities (I/I_1) and (hkl) assignments were taken from the data of Swanson and Tatge (25). It was found that the calcium hydroxide reflection corresponding to a d spacing of 0.8140 Å was incorrectly assigned. The (hkl) values should be (312) rather than (006).

For calcium oxide, plots of a_0 vs. $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$ (15) gave good straight lines, regardless of specific surface area and crystallite size. In the case of calcium hydroxide, there were not enough ($hk0$) and no ($00l$) reflections to permit single parameter evaluations. All unambiguous reflections in the range

d = 1.13 to 0.814 were, therefore, used, and a_0 and c_0 were obtained by least squares calculations (16). Statistical weights were assigned proportional to $(I/I_1)\tan^2\theta/d^2$, and the systematic errors were assumed to have the same angular dependence as those found for calcium oxide.

For the line broadening investigations, a scanning rate of $\frac{1}{8}$°/min. was used. The broadening of the calcium oxide line at 2.405 Å (100) and of the calcium hydroxide lines at 3.11 Å (100) and 4.91 Å (001) was measured. The crystallite dimensions were calculated by means of Scherrer's equation (22).

Other Operations

Ignition loss and carbon dioxide content were determined and chemical analyses were performed according to the methods described by Brunauer, Hayes, and Hass (4).

The calorimeter was essentially the same as that of Verbeck and Foster (28), with the modifications described by Brunauer, Kantro, and Weise (5). The acid solvent was 420 gm. of 2 N nitric acid.

Surface areas were measured by the B.E.T. method (3), using nitrogen at 77.3°K. Corrections for deviations from the perfect-gas law were taken from Emmett and Brunauer (8).

RESULTS

The experimental calorimetric results for calcium oxide and calcium hydroxide are shown in Table I. These results were then corrected for impurities.

TABLE I

HEATS OF SOLUTION OF CALCIUM OXIDE AND CALCIUM HYDROXIDE

CaO(A-40)		CaO (A-39)		$Ca(OH)_2$ (E-4)		$Ca(OH)_2$ (E-8)		$Ca(OH)_2$ (E-8A)	
Weight (gm.)	ΔH (cal./gm.)	Weight (gm.)	ΔH (cal./gm.)	Weight (gm.)	ΔH (cal./gm.)	Weight (gm.)	ΔH (cal./gm.)	Weight (gm.)	ΔH (cal./gm.)
1.0011	844.32	1.0043	847.54	0.6510	428.35	1.1506	428.02	1.0046	432.94
1.0065	845.42	1.0062	846.45	0.8255	427.26	1.2862	428.44	1.0100	432.77
1.0408	845.36	1.1379	848.16	0.8568	427.92	1.3668	427.63	1.0330	432.73
1.3427	844.99	1.3607	847.20	0.8866	428.68	1.3863	428.02	1.1325	432.17
1.3497	844.42	1.3624	846.51	1.0110	428.25	1.4760	427.97	1.3358	433.01
1.3503	844.26	1.3692	846.04	1.0198	427.67	1.5511	428.72	1.3606	432.32
1.3512	844.40	1.3828	847.66	1.0708	428.29				
1.3598	844.61			1.2286	427.39				
				1.2871	427.16				
				1.3673	428.71				
				1.4374	427.90				
				1.6253	428.13				
				1.7913	428.41				
Average = 844.72			847.08		428.01		428.13		432.66
Std. error = 0.17			0.29		0.14		0.18		0.16

Only impurities amounting to 0.01% or more were considered. Both batches of calcium oxide contained 0.01% sodium oxide; in addition, calcium oxide, Batch A-40, contained 0.05% magnesium oxide. The following impurities were found in the three batches of calcium hydroxide: in E-4, 0.01% sodium hydroxide and 0.13% calcium carbonate; in E-8, 0.01% sodium hydroxide, 0.07% magnesium hydroxide, 0.36% calcium carbonate, and 0.76% water; in E-8A, 0.01% sodium hydroxide, 0.07% magnesium hydroxide, 0.27% calcium carbonate, and 0.12% water. The following values were used for the

heats of solution of the impurities, in cal./gm.: sodium oxide, 1346; sodium hydroxide, 590; magnesium oxide, 865; magnesium hydroxide, 446; and calcium carbonate, 86. The corrections for water in calcium hydroxide, Batches E-8 and E-8A, will be discussed later.

Corrected values of the heats of solution, in cal./gm., exclusive of the heat evolved in the uptake of excess water, were as follows: calcium oxide, Batch A-40, 844.67; calcium oxide, Batch A-39, 847.03; calcium hydroxide, Batch E-4, 428.44; calcium hydroxide, Batch E-8, 432.64; and calcium hydroxide, Batch E-8A, 434.05.

Surface areas of the five substances, in meters^2/gm., were as follows: calcium oxide, Batch A-40, 0.3; calcium oxide, Batch A-39, 7.8; calcium hydroxide, Batch E-4, 0.1; calcium hydroxide, Batch E-8, 26.1; and calcium hydroxide, Batch E-8A, 21.8. It was assumed that one nitrogen molecule covered an area of 16.2 Å^2.

The two batches of calcium oxide gave identical values for the lattice parameter a, the edge of the unit cube, the value being 4.8108 ± 0.0002 Å. For the three batches of calcium hydroxide, the parameters of the hexagonal lattice were: Batch E-4, $a = 3.5933\pm0.0003$ Å, $c = 4.9086\pm0.0021$ Å; Batch E-8, $a = 3.5929\pm0.0006$ Å, $c = 4.9078\pm0.0046$ Å; and Batch E-8A, $a = 3.5926\pm0.0003$ Å, $c = 4.9082\pm0.0026$ Å. The determinations were made at 26°C.

The X-ray line broadening measurements gave the following results: On the basis of the half-intensity width of the 2.405 Å line of calcium oxide, Batch A-40, as standard, the broadening of that line of Batch A-39 was 0.030°2θ. With the half-intensity widths of the 3.11 and 4.91 Å lines of calcium hydroxide, Batch E-4, as standards, the broadening of the 3.11 Å lines of Batches E-8 and E-8A were 0.085 and 0.070°2θ, respectively; and the broadening of the 4.91 Å lines of E-8 and E-8A were 0.105 and 0.1325°2θ, respectively.

DISCUSSION

The Surface Energy of Calcium Oxide

1. In order to be reasonably certain that the energy difference between the two batches of calcium oxide was due to the difference between the specific surface areas *alone*, it had to be ascertained whether the bodies of the crystals had identical structures. This was accomplished (1) by precision determinations of the lattice parameter and (2) by X-ray line broadening measurements. The former showed that the lattice parameters a of the high and low surface calcium oxide were identical to the fifth significant figure. The identity is subject to an uncertainty of only 2×10^{-12} cm. in each determination, or one part in 24,000. Thus, the spacings of the ions in both batches of calcium oxide were found to be identical. The X-ray line broadening measurements, to be discussed in detail later, indicated that the crystals of both batches were either almost perfect, or, if not, the imperfections were of the same kind and extent.

2. The two batches of calcium oxide were prepared by widely differing methods: A-40 was "hard burned" lime, obtained by igniting calcium carbonate at 1300°C. for 64 hr., whereas A-39 was soft burned lime, obtained by igniting

calcium hydroxide at 1050°C. for 45 min. It is a well-known fact that hard burned lime reacts with water very slowly. The two batches of calcium oxide showed a marked disparity in their rates of reaction with 2 *N* nitric acid. It is clear from the X-ray results that this could not have been caused by differences in crystal densities (and, by implication, by differences in bond strengths), nor by crystalline imperfections. Very probably, the disparity in rate was caused by the difference between the specific surface areas of A-39 and A-40.

3. The corrected heat of solution of A-39 was 847.03 cal./gm., with a standard error of 0.17 cal./gm.; that of A-40 was 844.67 cal./gm., with a standard error of 0.29 cal./gm. The difference between the heats of solution was 2.36 cal./gm., with a standard error of 0.34 cal./gm. The surface area of A-39 was 7.8 meters²/gm.; that of A-40 was 0.3 meters²/gm. The difference was 7.5 meters²/gm., and the uncertainty in the difference was 0.1 meters²/gm. *The calculated surface energy of calcium oxide at 296°K. was 1310±200 erg/cm.²*

In addition to the errors mentioned above, there are two other possible sources of error to be considered. The molecular area of nitrogen at 77.3°K. was assumed to be 16.2 Å². Livingston (19) proposed an area of 15.4 Å². If Livingston's figure is correct, the surface energy of calcium oxide is 70 erg/cm.² *higher* than the value given above. The area of 16.2 Å² was used by Brunauer, Emmett, and Teller (3), and it was confirmed by Harkins and Jura (12) by means of a totally different approach.

A second source of error may have come from an uptake of water by calcium oxide, Batch A-39, during the introduction of the sample into the calorimeter. In the experimental part, the method used to estimate the magnitude of this effect was described. It is possible that no water was picked up during the less than five seconds of addition; if there was any uptake, it was at most about 0.13 mgm./gm. (A monolayer of water would correspond to 2.20 mgm./gm., using a molecular area of 10.6 Å².) Jura and Garland (14) found that when magnesium oxide sorbed an amount of water sufficient to form half a monolayer, the heat evolved per mole of water was about equal to the heat of hydration of magnesium oxide. If it is assumed that the same is true for calcium oxide, the heat evolved in the sorption of 0.13 mgm. of water would be 0.11 cal. A correction for this effect would *raise* the surface energy of calcium oxide by 60 erg/cm.²

The above errors may or may not exist, but even if they do, they are relatively small. If both were present, the surface energy would be raised by a *maximum* of 130 erg/cm.² Not knowing whether or not these errors were present, no attempt was made to correct for them. It is clear, however, that a more cautious estimate of the surface energy of calcium oxide would be 1375± 250 erg/cm.²

4. Lennard-Jones and Taylor (17) calculated the surface energy of the (100) face of calcium oxide at 0°K. and obtained 1032 erg/cm.² Jura and Garland found experimentally that the surface energy of magnesium oxide increased by 50 erg/cm.² in the temperature range from 0° to 298°K. Because of the similarity between calcium oxide and magnesium oxide, it may safely be

assumed that the surface energy of calcium oxide at room temperature is also larger than the 0°K. value by the same amount. Thus, the theoretical surface energy of calcium oxide at 23° would be about 1100 erg/cm.^{2} The experimental value is 1310±200 erg/cm.^{2} The agreement between theory and experiment is, therefore, quite good.

The agreement between the experimental and theoretical surface energy of magnesium oxide is reasonably good. Jura and Garland obtained 1100 erg/cm.^{2} for the former, and Lennard-Jones and Taylor obtained 1362 erg/cm.^{2} for the latter. The value of Jura and Garland is probably too low. Since the surface energy of even calcium hydroxide appears to be greater than 1100 erg/cm.^{2}, it seems improbable that that of calcium oxide should be less than this value. On the basis of theory, the surface energy of magnesium oxide should be about 300 erg/cm.^{2} larger than that of calcium oxide, or at least 1400 erg/cm.^{2} Jura and Garland pointed out that they were unable to estimate the amount of water picked up by the magnesium oxide samples in the course of introducing them into the calorimeter. It is possible that their high surface magnesium oxide picked up enough water and carbon dioxide from the atmosphere to account for the somewhat low result.

The agreement between the theoretical and experimental surface energies of calcium oxide and magnesium oxide is so much the more surprising, since the experimental surface energy obtained for sodium chloride is twice as large as the best theoretical value, calculated by Shuttleworth (23).* Recently, van der Hoff and Benson (13) calculated the surface energy of lithium fluoride on the basis of a quantum mechanical model, instead of the "classical" model used by earlier investigators. They obtained a surface energy value almost three times as large as that based on the classical model. It seems that it would be desirable to recalculate the surface energies of calcium oxide and magnesium oxide on the basis of quantum mechanical models.

The Surface Energy of Calcium Hydroxide

1. The lattice parameters of the three batches of calcium hydroxide were given under "Results". The precision attained in the evaluation of the two parameters was somewhat smaller than that obtained for the single lattice parameter of calcium oxide. Since the differences are not statistically significant, it can be concluded that all three batches of calcium hydroxide had the same a and the same c parameters, indicating the same spacings of the ions in the crystals. The X-ray line broadening measurements, to be discussed in detail later, indicated that the crystals of all three batches were either almost perfect or, if not, the imperfections were of the same kind and extent.

In spite of the above facts, the differences between the heats of solution of E-4 and E-8 on the one hand, and between E-4 and E-8A on the other, were not caused by differences in surface energy *alone*. Both E-8 and E-8A contained some excess water, and the differences between the heats of solution were

**G. C. Benson and R. McIntosh (Can. J. Chem. 33: 1677. 1955) recently pointed out that the agreement between the theoretical value of Lennard-Jones and Taylor and the experimental value of Jura and Garland for the surface energy of magnesium oxide is probably fortuitous. In the theoretical calculations, the van der Waals term was neglected and the repulsive term was calculated in a questionable manner. The same criticism applies to the theoretical calculation of the surface energy of calcium oxide.*

partly caused by the heat of sorption of water. It is possible that the water was occluded in the lattice, and it is possible that it was adsorbed on the surface. Corrections for the water were attempted both ways and, as will be seen, both types of correction led to the same result.

2. Calcium hydroxide, Batch E-4, contained no excess water, Batch E-8A contained 0.12%, and Batch E-8 contained 0.76% excess water. The fact that the lattice parameters of the three batches were the same made it unlikely that the water was dissolved in the lattice. Nevertheless, it is possible that some water can be dissolved in the calcium hydroxide lattice without changing its dimensions, and it is also possible that the dimensions of the three batches were actually slightly different, even though in the present experiments the differences could not be detected. At any rate, calculations were made on the basis of the assumption that the water was dissolved in the lattices of E-8 and E-8A.

The corrected heat of solution of E-4 was 428.44 cal./gm.; the heats of solution of E-8 and E-8A, corrected for all impurities but uncorrected for the heat of sorption of excess water, were 432.64 and 434.05 cal./gm., respectively. The surface areas of E-4, E-8, and E-8A were 0.1, 26.1, and 21.8 meters^2/gm., respectively. By assuming that the heat evolved in the solution of water in the calcium hydroxide lattice is proportional to the amount of water dissolved, one can calculate from the above data both the heat of solution of water and the surface energy. The heat evolved in the solution was found to be 412 cal./gm. of water (or 7420 cal./mole of water), and the surface energy of calcium hydroxide was 1180 erg/cm.^{2}

3. It seems more likely that the excess water in Batches E-8 and E-8A was adsorbed water. Since there are no data available on the heats of adsorption of water on calcium hydroxide, the values were estimated on the basis of the fact that the heats of physical adsorption of water on a variety of surfaces show striking similarities.

The amount of excess water in Batch E-8 corresponded to a monolayer of adsorbed water, provided the area of a water molecule is assumed to be 10.3 Å^2. Although this value is somewhat smaller than the 10.6 Å^2 obtained from the density of liquid water, such a close packing on the surface does not seem unreasonable. Harkins and Jura (11) found that the integral net heat of adsorption of water on anatase (titanium dioxide), at an amount of water adsorbed equal to a monolayer, was 6550 cal./mole of water. Copeland (6) found in this laboratory that the integral net heat of adsorption of water on *hydrated* portland cement under the same condition was 6640 cal./mole. If one takes the average, 6600 cal./mole, as a reasonable value for the integral net heat of adsorption of water on calcium hydroxide at an adsorption equal to a monolayer, the water correction of the heat of solution of Batch E-8 is 2.78 cal./gm. This value is to be added to the difference between the heats of solution of E-8 and E-4, 4.20 cal./gm. The difference between the surface areas of E-4 and E-8 was 26.0 meters^2/gm. The calculated surface energy of calcium hydroxide was 1120 erg/cm.^{2}

As stated earlier, the heating of E-8 resulted in some sintering, the surface area decreasing from 26.1 to 21.8 meters^2/gm. If one assumes a molecular

area of 10.3 Å^2 for water, 6.33 mgm. of water would cover 1 gm. of E-8A with an adsorbed monolayer. The water content of E-8A was 1.2 mgm. per gm., corresponding to a surface coverage of 19%. The heat of adsorption of this water was estimated in the following manner. The integral net heat of adsorption of water on various surfaces was plotted against θ, the fraction of the surface covered. The data of Harkins and Jura (11) for anatase, those of Powers and Brownyard (21) and Copeland (6) for hydrated portland cement, and some data by the authors of this paper for hydrated tricalcium silicate fell on a single curve. The integral net heat of adsorption at $\theta = 0.19$ was 12,500 cal./mole. Assuming that this is a reasonable value for a calcium hydroxide surface as well, the water correction of the heat of solution of Batch E-8A is 0.83 cal./gm. This value is to be added to the difference between the heats of solution of E-8A and E-4, 5.61 cal./gm. The difference between the surface areas of E-8A and E-4 was 21.7 meters^2/gm. The calculated surface energy of calcium hydroxide was 1240 erg/cm.^{2}

The surface energy obtained from the data on E-4 and E-8 was found to be 1120 erg/cm.^{2}, and that obtained from the data on E-4 and E-8A was 1240 erg/cm.^{2} The average of the two is 1180 erg/cm.^{2} The value obtained on the basis of the assumption that the excess water was dissolved in the lattice of calcium hydroxide was also 1180 erg/cm.^{2}

4. Whether the excess water was dissolved or adsorbed, the conclusion is that *the surface energy of calcium hydroxide at 296°K. is 1180 erg/cm.^{2} The uncertainty, estimated below, is ±100 erg/cm.^{2}*

The standard errors of the average heats of solution for the three batches of calcium hydroxide were given in Table I. The standard error in the surface area of Batches E-8 and E-8A is ±0.2 meters^2/gm. These errors lead to an uncertainty of ±50 erg/cm.^{2} in the surface energy. Uncertainties in the corrections for impurities other than water introduce an additional error of ±15 erg/cm.^{2} The error in the water correction may be as high as 40 erg/cm.^{2} For the heat of adsorption of water on E-8A the value of 12,500 cal./mole was assumed. The heat of adsorption of water on calcium hydroxide is probably not as high as the heat of reaction of calcium oxide with water; nevertheless, if the value of 15,600 cal./mole is used for the heat of adsorption, the surface energy of calcium hydroxide calculated from the data of E-8A would be raised by 40 erg/cm.^{2}

The above errors together amount to an uncertainty of about 100 erg/cm.^{2} This does not take into account the uncertainty in the molecular area of nitrogen, discussed before. If Livingston's (19) value is correct, the surface energy of calcium hydroxide would be raised by 5%, or about 60 erg/cm.^{2} Nor does the 100 erg/cm.^{2} error include the possible error caused by an uptake of water during the introduction of the calcium hydroxide into the calorimeter. This error may amount to as much as 15 erg/cm.^{2} A cautious estimate of the surface energy of calcium hydroxide would be 1220±150 erg/cm.^{2}

5. The only surface energy value in the literature with which the present value for calcium hydroxide can be compared is that obtained by Fricke, Schnabel, and Beck (9) for magnesium hydroxide. Their value of 330 erg/cm.^{2}

seems to be too low by a factor of 3, at least. They estimated the specific surface areas of their magnesium hydroxide samples by means of X-ray line broadening measurements, and the greatest part of the line broadening may have been caused by crystalline imperfections, rather than by dimensions. This point will be further discussed later.

One would intuitively expect that the surface energy of calcium hydroxide should be somewhere between the surface energies of calcium oxide, 1310 erg/cm.^{2}, and water, 118.5 erg/cm.^{2} (11). (There is no surface energy value available for ice.) The value of 1180 erg/cm.^{2} is actually between those limits, and it is quite close to the surface energy of calcium oxide. Perhaps this result is not too surprising. The non-specificity that one finds in physical adsorption is primarily due to the fact that the predominating factor is the change in the state of the adsorbate. Nevertheless, when one encounters such a ***high degree*** of non-specificity as found, for example, in the already discussed heats of adsorption of water on *anhydrous* and *hydrated* surfaces, the cause is probably to be found not merely in the identity of the adsorbate but also in the similarities between the surface energies of the adsorbents. Likewise, such dissimilarities as were found, for example, by Harkins and Boyd (10) in the heats of wetting of various ionic surfaces by water were probably caused by dissimilarities in the energies (both free and total) of those surfaces.

6. Jura and Garland (14) found that the free surface energy of magnesium oxide was 90 erg/cm.^{2} less than its total surface energy at room temperature. Because of the similarity of calcium oxide to magnesium oxide, it is probable that the free surface energy of calcium oxide is also about 100 erg/cm.^{2} less than its surface energy, or about 1200 erg/cm.^{2} In general, the entropies of solid surfaces seem to be low; thus, at room temperature the free surface energy differs only slightly from the total surface energy. A value of 1100 erg/cm.^{2} for the free surface energy of calcium hydroxide is probably close to the true value.

X-Ray Line Broadening and Surface Area

1. The broadening of X-ray diffraction lines is caused either by crystalline imperfections, such as, for example, mosaic structure (7), or by small dimensions of the crystals. Scherrer (22) was the first to show how mean dimensions of the crystallites can be calculated from line broadening. Naturally, this can be done only if the broadening caused by imperfections is negligible compared to the broadening caused by crystal size. This appeared to be true or nearly true for the calcium oxide and calcium hydroxide crystals used in the present investigations, since the surface areas calculated from line broadening measurements were, within the errors involved, about the same as those obtained from nitrogen adsorption.

2. The 2.405 Å line of calcium oxide is the (100) reflection; the dimension calculated from the broadening of this line is, therefore, that of the edge of the average cube. It follows from Scherrer's formula that

$$\frac{B}{93.11} = \frac{1}{D_{A\text{-}39}} - \frac{1}{D_{A\text{-}40}}$$

where B is the difference between the half intensity widths of the 2.405 Å lines of A-39 and A-40 in degrees of 2θ, and $D_{A\text{-}39}$ and $D_{A\text{-}40}$ are the lengths of the edges of the average cubes of A-39 and A-40 in Ångstrom units, respectively.

Using 3.345 gm./cc. for the density of calcium oxide and 0.3 meters^2/gm. for the specific surface area of A-40, one obtains the value of 5.98 μ for $D_{A\text{-}40}$. Since $B = 0.030°$ (see "Results"), $D_{A\text{-}39} = 2950$ Å. If it is assumed that A-39 was composed of cubes of equal sizes, calculation leads to the results that (*a*) 1 gm. of A-39 contained 1.16×10^{13} cubes, and (*b*) the specific surface area was 6.1 meters^2/gm. The surface area obtained by nitrogen adsorption was 7.8 meters^2/gm. Thus, line broadening indicated a surface area 22% *smaller* than nitrogen adsorption did.

3. Similar calculations were made for the two high-surface calcium hydroxide batches, E-8 and E-8A. In this case, it was assumed that the calcium hydroxide crystallites were hexagonal prisms, and the height of the average prism was obtained from the broadening of the 4.91 Å line (001), and the side of the hexagon was calculated from the broadening of the 3.11 Å line (100). The density of calcium hydroxide was taken to be 2.241 gm./cc., and the specific surface area of E-4 (used as standard), 0.1 meters^2/gm. The height of the average prism was found to be 845 Å for E-8 and 670 Å for E-8A, and the side of the average hexagon 1230 Å for E-8 and 1495 Å for E-8A. If it is assumed that E-8 was composed of hexagonal plates of equal sizes, and a similar assumption is made for E-8A, calculations lead to the results that (*a*) 1 gm. of E-8 contained 1.34×10^{14} and 1 gm. of E-8A, 1.15×10^{14} plates, and (*b*) the specific surface area of E-8 was 18.9 and that of E-8A, 20.2 meters^2/gm. The specific surface areas thus obtained for E-8 and E-8A are *smaller* than the nitrogen adsorption areas by 28 and 7%, respectively.

4. It is to be noted that in all three instances line broadening gave smaller surface areas than nitrogen adsorption did. The reason for this is found in the fact, experimentally demonstrated by Birks and Friedman (2), that line broadening gives greater weights to the large particles than to the small ones. It seems clear from their results, as well as from the present data, that the surface area calculated from the average dimensions, obtained from X-ray line broadening, will, in general, be smaller than the true surface area for polydisperse systems, *provided that the line broadening is caused by the dimensions of the crystals alone*. Line broadening can give an accurate value for the surface area only for monodisperse systems, just as nitrogen adsorption can give the correct particle size only for monodisperse systems.

In the majority of cases published in the literature, the surface areas calculated from line broadening were *larger* than those determined by nitrogen adsorption. It is very likely that in these instances the broadening was not caused by crystal size alone but by a combination of size and crystalline imperfections.

5. It follows from the above considerations that care must be exercised in calculating surface areas from line broadening. For example, the large apparent surface area value obtained by Fricke, Schnabel, and Beck (9) for magnesium hydroxide, discussed earlier, was probably caused by imperfections in the

crystals. Another example is found in some of the results obtained for calcium hydroxide, Batches E-8 and E-8A. The latter was obtained by heating the former at 180° to 200° for 16 hr. The nitrogen adsorption clearly indicated sintering, the surface area having decreased from 26.1 to 21.8 meters²/gm. However, the surface area calculated from line broadening showed a reverse effect; it increased on heating from 18.9 to 20.2 meters²/gm. This is, obviously, a false result.

6. Nevertheless, some interesting speculations can be made on the basis of the line broadening measurements. Heating resulted in a decrease in the number of crystallites per gram of calcium hydroxide by about 14%. This is an indication of sintering. The crystallites that disappeared must have been the smallest ones. The resulting material must have been more nearly monodisperse than the initial material, from which it follows that there should be a better agreement between the X-ray surface and the nitrogen surface for E-8A than for E-8. This was actually true; the X-ray surface of E-8 was 28% smaller than the nitrogen surface, whereas the X-ray surface of E-8A was only 7% smaller. The agreement between the X-ray surface and the nitrogen surface obtained for E-8A is quite striking. It would become even more striking if one would use Livingston's (19) value for the adsorption area of a nitrogen molecule. In that case the two would differ only by 2%.

The slight sintering resulted in some flow of the material. Line broadening showed that the flat plates had become thinner; the average height of the hexagonal plates of E-8 was 845 Å, that of E-8A was 670 Å.

7. All dimensions in this section were calculated by means of Scherrer's formula (22). Warren (29) also proposed a formula for the calculation of crystal dimensions from line broadening. For calcium oxide, Batch A-39, Scherrer's formula led to a value of 2950 Å for the edge of the average cube, whereas Warren's formula led to 860 Å. The former value gave a surface area 22% smaller than the nitrogen adsorption area, the latter gave an area 2.8 times larger. It seems, therefore, that for the types of systems investigated, Warren's formula is not applicable. No attempt was made to use the method of Stokes (24).

The Heat of Hydration of Calcium Oxide

A by-product of the present investigations was a value for the heat of the reaction

$$CaO\ (c,\ 23°) + H_2O(l,\ 23°) = Ca\ (OH)_2\ (c,\ 23°)$$

for the case when both the calcium oxide and calcium hydroxide crystals have negligible surface areas. The heat of solution of calcium oxide, Batch A-40, was 844.67 cal./gm. The surface area of this batch was 0.3 meters²/gm. Correcting to zero surface gave a heat of solution of 844.58 cal./gm. The heat of solution of calcium hydroxide, Batch E-4, was 428.44 cal./gm., and the surface area was 0.1 meters²/gm. Correcting to zero surface gave a heat of solution of 428.42 cal./gm. From these values, it follows that

$$\Delta H_{296} = -15{,}620 \text{ cal.}$$

The estimated uncertainty is ±20 cal. Thorvaldson, Brown, and Peaker (27) obtained the value of −15,640 cal. for ΔH_{293} by determining the heats of solution of calcium oxide and calcium hydroxide in hydrochloric acid, and −15,490 cal., by measuring directly the heat evolved in the hydration of calcium oxide. They gave preference to the former value, and the present result confirms the correctness of their choice.

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AMINO ACIDS

III. CYCLIC GUANIDINO ACIDS AND THEIR DERIVATIVES[1]

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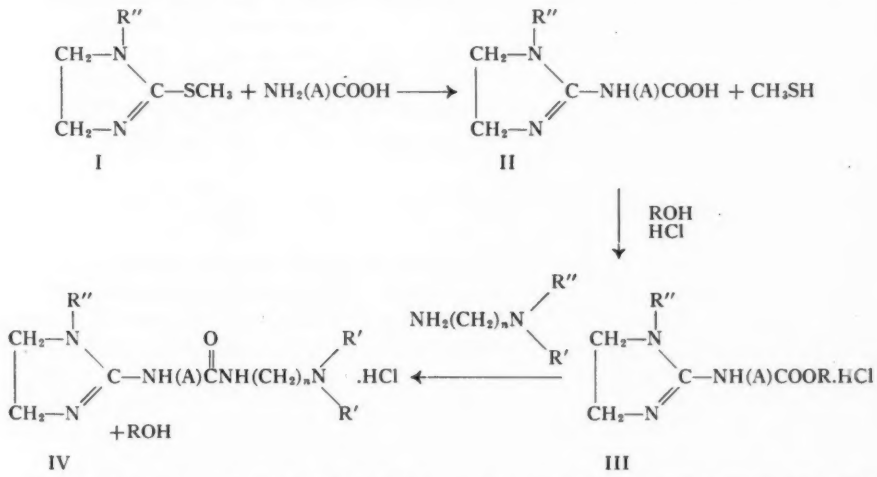
ABSTRACT

Several new cyclic guanidino acids have been prepared by the reaction of cyclic isothioureas with amino acids. The ethyl esters of some of these acids have been converted into dialkylaminoalkylamides by refluxing with dialkylaminoalkylamines in the presence of an inert solvent. A series of dialkylaminoethyl esters of the 2-(carboxyalkylamino)-2-imidazolines also have been prepared.

The reaction (3) of amino acids with cyclic isothioureas (I) provides a convenient method for the preparation of 2-(carboxyalkylamino)-2-imidazolines (II) (or the tautomeric 2-(carboxyalkylimino)-imidazolidines). These imidazoline derivatives are prepared most conveniently in the laboratory by refluxing the free base of a 2-methylmercapto-2-imidazoline and an amino acid in the presence on an inert solvent such as methanol or benzene. In this manner, the products have been obtained in yields as high as 96%.

Some difficulty has been experienced with the esterification of the 2-(carboxyalkylamino)-2-imidazolines (II). The yields of ester hydrochlorides (III) vary considerably although yields as high as 83% have been obtained. A



A = alkylene group R = alkyl or dialkylaminoethyl R′ = alkyl R″ = H or $-CH_2CH_2OH$

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[3]*Ayerst, McKenna and Harrison Limited.*

number of dialkylaminoethyl esters of the 2-(carboxyalkylamino)-2-imidazolines also have been prepared. These are described fully in the Experimental section.

The ethyl esters of the 2-(carboxyalkylamino)-2-imidazolines are converted into the corresponding amides (IV) by refluxing with amines in the presence of inert solvents. The amides are very difficult to purify as free bases. They are generally waxy light brown solids, so their dipicrates have been prepared for identification.

EXPERIMENTAL[4]

γ-Aminobutyric Acid

A solution of 2-pyrrolidone[5] (212.5 gm., 2.50 mole) and anhydrous barium hydroxide (223.3 gm., 1.30 mole) in 1 liter of water was heated at 100°C. for two hours. The solution was cooled, a few drops of concentrated hydrochloric acid added, and the solution was neutralized with 2.3 *N* sulphuric acid (1129 cc.). The suspension was boiled for 30 min. and then allowed to stand overnight. The barium sulphate was filtered (with the aid of Celite) and the filtrate, on evaporation, gave 200 gm. (78%) of crude product. One crystallization from ethyl alcohol (2 liters) yielded 170 gm. (68%) of product melting at 198–198.5°C.

ε-Aminocaproic Acid

A solution of ε-caprolactam[6] (113 gm., 1.0 mole) and anhydrous barium hydroxide (95.0 gm., 0.55 mole) in 1500 cc. water was heated at 100°C. for two hours. The solution was cooled, a few drops of concentrated hydrochloric acid were added, and the solution was neutralized by dropwise addition of 3 *N* sulphuric acid (370 cc.). The suspension of barium sulphate was boiled for 10 min., and then allowed to settle overnight. The precipitate was removed by filtration and the filtrate was evaporated, yield 120 gm. (92%). This crude residue was crystallized from ethyl alcohol (1 liter) to give 100 gm. (76.5%) of material melting at 200–202°C.

2-(γ-Carboxypropylamino)-2-imidazoline

Method A

A solution of 2-methylmercapto-2-imidazolinium iodide (1) (244 gm., 1.0 mole), γ-aminobutyric acid (98.0 gm., 0.95 mole), and sodium hydroxide (80 gm., 2.0 mole) in 2 liters of water was allowed to stand at room temperature for three days. The evolved methyl mercaptan was absorbed in 20% sodium hydroxide solution. At the end of the reaction period, the solution was diluted to a volume of 6 liters with water and it was passed through a column of mixed-bed resin (2 liters of Amberlite IRA–400[7] activated resin and 2 liters of Amberlite IRC-50 resin[7]) at a rate of 20 cc. per min. The column was washed with water and the combined eluate and washings were evaportaed *in vacuo*. The semicrystalline residue weighed 130 gm. (80% yield). Crystallization from methanol (300 cc.) gave 100 gm. of white crystals melting at 185–224°C.

[4]*All melting points are uncorrected. Microanalyses by C. W. Beazley, Skokie, Illinois, and Drs. Weiler and Strauss, Oxford, England.*
[5]*General Aniline and Film Corp., New York, N.Y.*
[6]*Dupont Co. of Canada Limited, Montreal, Que.*
[7]*Rohm and Haas Company, Philadelphia, Penn., U.S.A.*

Another crystallization from methanol raised the melting point to a constant value of 224–225°C. Calc. for $C_7H_{13}N_3O_2$: C, 49.10; H, 7.65; N, 24.52%. Found: C, 48.78; H, 7.99; N, 24.75%. Its picrate, which was formed in aqueous solution, melted at 171–172°C. after crystallization from alcohol. Calc. for $C_{13}H_{16}N_6O_9$: C, 38.99; H, 4.03; N, 21.00%. Found: C, 38.79; H, 3.88; N, 21.18%.

Method B

A solution of 2-methylmercapto-2-imidazolinium iodide (122 gm., 0.5 mole) in 500 cc. of water was passed through a column of Amberlite IRA–400 resin (1 liter) at a rate of 7 cc. per min. and then the column was washed with 2 liters of water. γ-Aminobutyric acid (50.0 gm., 0.49 mole) was added to the total eluate and the solution was allowed to stand in the fume-hood at room temperature for 60 hr. An amorphous residue (79 gm., 95% yield)was obtained from evaporation of this solution *in vacuo*. One crystallization from methanol (200 cc.) gave pure 2-(γ-carboxypropylamino)-2-imidazoline (m.p. 224–225°C.). This product did not depress the melting point of a sample of the acid prepared by method A. The methanolic mother liquor on evaporation gave 12 gm. of oily residue. This oil has not been identified.

Method C

2-Methylmercapto-2-imidazolinium iodide (24.4 gm., 0.10 mole) was added to a solution of potassium hydroxide (11.4 gm., 0.20 mole) in 12 cc. of water. This solution was extracted with ether (4×50 cc.) and the ethereal solution was evaporated. Nine grams (77.5%) of the free base, 2-methylmercapto-2-imidazoline, was obtained. The 2-methylmercapto-2-imidazoline and γ-aminobutyric acid (7.5 gm., 0.073 mole) in methanol (100 cc.) were refluxed for two hours until the evolution of methylmercaptan had ceased. When the solution was concentrated *in vacuo*, 12 gm. (96% yield based on γ-aminobutyric acid) of 2-(γ-carboxypropylamino)-2-imidazoline (m.p. 223–225°C.) was obtained.

1-(β-Hydroxyethyl)-2-(γ-carboxypropylamino)-2-imidazoline

γ-Aminobutyric acid (64.3 gm., 0.62 mole), 1-(β-hydroxyethyl)-2-methylmercapto-2-imidazolinium iodide (4) (179.4 gm., 0.60 mole), and sodium hydroxide (25.0 gm., 0.62 mole) were dissolved in 3 liters of water and this solution was allowed to stand at room temperature for three days. After the reaction was complete, the solution was processed as described in method A above for 2-(γ-carboxypropyl)-2-imidazoline. The crude product (94 gm., 77% yield) was purified to constant melting point of 204.5–205.5°C. by crystallization from methanol, yield 36.0 gm. Calc. for $C_9H_{17}N_3O_3$: C, 50.22; H, 7.97; N, 19.53%. Found: C, 50.21; H, 8.12; N, 19.80%.

1-(β-Hydroxyethyl)-2-(ε-carboxypentylamino)-2-imidazoline

1-(β-Hydroxyethyl)-2-methylmercapto-2-imidazolinium iodide (115.2 gm., 0.40 mole) in 62 cc. of absolute ethanol was added to a 2.42 *N* absolute ethanolic potassium hydroxide solution at 0°C. Ether (680 cc.) was added and the precipitated potassium iodide (65.3 gm., 98.2% yield) was removed by filtration. ε-Aminocaproic acid (46 gm., 0.35 mole) was added to the filtrate and the ether was removed by distillation. The residual alcoholic solution was refluxed for six hours until the evolution of methylmercaptan ceased. The alcoholic

solution on cooling gave 66.2 gm. (78%) of crude product which melted at 188–195°C. Crystallization from methanol (6 cc. per gm.) raised the melting point to a constant value of 209–210°C. Calc. for $C_{11}H_{21}N_3O_3$: C, 54.20; H, 8.70; N, 17.28%. Found: C, 54.25; H, 8.76; N, 16.80%.

2-(γ-Carbethoxypropylamino)-2-imidazoline

A solution of 2-(γ-carboxypropylamino)-2-imidazoline (17.1 gm., 0.1 mole) in ethanol (150 cc.) containing 0.3 mole of hydrogen chloride was refluxed for two hours. Benzene (50 cc.) was added and the refluxing was continued another hour. The benzene was distilled from the solution to remove water as the benzene–water–alcohol azeotrope. This procedure was repeated twice more and then the solution was taken to dryness, yield 21.0 gm. (89.5%). A sample of this product in aqueous solution was converted into its picrate. Its melting point was raised from 104–108°C. to 114–115°C. by three crystallizations from 50% aqueous ethanol. Calc. for $C_{15}H_{20}N_6O_9$: C, 42.02; H, 4.71; N, 19.62%. Found: C, 42.19; H, 4.65; N, 19.9%.

2-(N-γ-Dimethylaminopropyl-γ-carbamylpropylamino)-2-imidazoline

The above-described 2-(γ-carbethoxypropylamino)-2-imidazolinium chloride (20.5 gm., 0.087 mole) and γ-dimethylaminopropylamine (10.4 gm., 0.1 mole) were dissolved in absolute ethanol (200 cc.) and this solution was refluxed for four hours. Then the solution was evaporated to dryness and the residue was dissolved in 300 cc. of water. This aqueous solution was passed through a column of activated Amberlite IRA-400 resin (400 cc.) and the column was washed with water (1 liter). On evaporation the eluate gave 5.5 gm. (24.7%) of a brown gummy solid. This solid, its mono- and its di-hydrochlorides, could not be purified by crystallization. Its picrate formed from aqueous solution melted at 155–155.5°C. Calc. for $C_{24}H_{31}N_{11}O_{15}$: C, 40.38; H, 4.38; N, 21.6%. Found: C, 40.37; H, 4.56; N, 21.82%.

β-Diethylaminoethylamine

N,N-Diethyl ethylenediamine (b.p. 146–150°C. at 760 mm.; $n_D^{25} = 1.4345$) was obtained in 41% yield by the method of Braz and Skorodumov (2). This reaction also gave a 21.8% yield of N,N-diethyl-N′-(2-aminoethyl) ethylenediamine ($n_D^{27} = 1.4572$) as well as higher addition products.

2-(N-β-Diethylaminoethyl-γ-carbamylpropylamino)-2-imidazoline

A solution of 2-(β-carbethoxyethylamino)-2-imidazolinium chloride (7.34 gm., 0.029 mole) and β-diethylaminoethylamine (3.4 gm., 0.029 mole) in 60 cc. of absolute ethanol was refluxed for four hours. After evaporation, this solution gave 9.0 gm. (95%) of amorphous material. The residue was dissolved in methanol (100 cc.) and the methanolic solution was passed through a column of Amberlite IRA-400 resin (150 cc.). After the column was washed with methanol (450 cc.), the total eluate was evaporated. The oily residue weighed 3.2 gm. (35.6%). It could be crystallized from ethyl acetate (8 cc.) to give a gummy reddish solid. A picrate formed from this solid melted at 135–135.5°C. Calc. for $C_{25}H_{33}N_{11}O_{15}$: C, 41.26; H, 4.57; N, 21.2%. Found: C, 41.11; H, 4.36; N, 21.28%.

2-(N-γ-Dimethylaminopropylcarbamylmethylamino)-2-imidazoline (VI)

2-(Carbethoxymethylamino)-Δ^2-1,3-diazacyclopentene hydrochloride (3) (4.23 gm., 0.02 mole) and 2.08 gm. (0.02 mole) of N,N-dimethylaminopropylamine were refluxed in the presence of 40 cc. of absolute ethanol for four hours. On cooling in the refrigerator, a white solid separated, yield 0.658 gm. (22.5%). This solid melted at 280°C. with decomposition. It was identified as the free acid 2-(carboxymethylamino)-Δ^2-1,3-diazacyclopentene, by a comparison of their infrared absorption spectra. The ethanolic filtrate from the free acid was taken to dryness *in vacuo*. The residue was a viscous oil, which crystallized on standing, yield 4.09 gm. (74.8% as the monohydrochloride). A small sample of this solid was precipitated as its picrate from its aqueous solution. Two crystallizations from water raised the melting point from 167°C. to 189.5–191°C. Anal. Calc. for dipicrate $C_{22}H_{27}N_{11}O_{15}$: C, 38.52; H, 3.97; N, 22.48%. Found: C, 38.11; H, 4.14; N, 22.25%.

Dimethylaminoethyl Ester of 2-(ε-Carboxypentylamino)-2-imidazolinium Chloride Monopicrate

2-(ε-Carboxypentylamino)-2-imidazoline (3) (9.9 gm., 0.05 mole) and dimethylaminoethanol (4.5 gm., 0.05 mole) were suspended in 150 cc. of toluene and heated at 140°C. for 10 hr. During the heating period dry hydrogen chloride was bubbled through the solution and toluene was distilled over slowly. Fresh toluene was added at intervals as required. On cooling, the toluene was decanted and the oily residue was converted into its picrate in aqueous solution, yield 17 gm. (63.5%). The melting point of this picrate was raised from 183–185°C. to 186–187.5°C. by one crystallization from ethanol. Calc. for $C_{19}H_{30}ClN_7O_9$: C, 42.65; H, 5.63; Cl, 6.62; N, 18.30%. Found: C, 43.02; H, 5.57; Cl, 6.75; N, 18.28%.

Dimethylaminoethyl Ester of 2-(γ-Carboxypropylamino)-2-imidazolinium Chloride Monopicrate

The dimethylaminoethyl ester of 2-(γ-carboxypropylamino)-2-imidazoline chloride monopicrate (m.p. 183–185°C.) was prepared in 46.3% yield by the above procedure. One crystallization from acetonitrile raised the melting point to a constant value of 188–189°C. Calc. for $C_{17}H_{26}ClN_7O_9$: C, 40.25; H, 5.16; Cl, 6.98; N, 19.35%. Found: C, 40.44; H, 5.15; Cl, 6.73; N, 19.25%.

Dimethylaminoethyl Ester of 2-(Carboxymethylamino)-2-imidazoline Dipicrate

The above esterification procedure gave the dipicrate of the dimethylaminoethyl ester of 2-(carboxymethylamino)-2-imidazoline (m.p. 152–156°C.) in 48.0% yield. Two crystallizations from acetonitrile raised the melting point to 161.5–165.5°C. Calc. for $C_{21}H_{24}N_{10}O_{16}$: C, 37.55; H, 3.37; N, 20.85%. Found: C, 37.85; H, 3.46; N, 20.57%.

In a similar manner the following dialkylaminoalkyl esters of 2-(ε-carboxypentylamino)-2-imidazoline were prepared.

Diisopropylaminoethyl Ester of 2-(ε-Carboxypentylamino)-2-imidazoline Dipicrate

M.p. 127–130°C.; yield 86.6%. Calc. for $C_{29}H_{40}N_{10}O_{16}$: C, 44.35; H, 5.14; N, 17.85%. Found: C, 44.76; H, 5.08; N, 17.78%.

Diethylaminoethyl Ester of 2-(ε-Carboxypentylamino)-2-imidazoline Dipicrate

M.p. 120–123°C.; yield 68.8%. Calc. for $C_{27}H_{36}N_{10}O_{16}$: C, 42.85; H, 4.79; N, 18.51%. Found: C, 43.15; H, 4.51; N, 18.49%.

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THE DISTRIBUTION OF PLUTONIUM IN THE SYSTEMS URANIUM–SILVER AND URANIUM–SILVER–GOLD[1]

By D. E. McKenzie

ABSTRACT

An expression due to Hildebrand and Scott has been used to select silver as a possible extractant for plutonium from neutron-irradiated uranium. The distribution of plutonium between molten silver and molten neutron-irradiated uranium has been examined in small-scale experiments. The fraction of plutonium in the silver layer increases with increasing temperature. For equal weights of silver and uranium containing 0.1% plutonium, 88% of the total plutonium is distributed to the silver phase at 1350°C. Greater proportions of plutonium are found in the silver phase in experiments with uranium of lower initial plutonium concentration. On the addition of gold to the system plutonium extraction is increased and passes through a maximum. This maximum appears to be associated with a particular concentration of gold in silver and of gold in uranium.

INTRODUCTION

A cheap and simple method for the separation of plutonium from neutron-irradiated uranium may be important to the development of cheap nuclear power. One approach of some promise for metallic uranium fuels is to achieve the separation while retaining the uranium as metal. The volatilization of plutonium from neutron-irradiated uranium was described in a previous paper (3) as an example of this approach. A second possible technique makes use of the principle of molten metal extraction. In this method plutonium is extracted from molten uranium into a metal which is essentially immiscible with uranium. As the extracting metal, silver has shown considerable promise. The theoretical background used for the selection of silver and some of the results obtained with this metal are described in this paper. The use of silver has also been considered by Dr. F. H. Spedding and co-workers at the Ames laboratory of the United States Atomic Energy Commission. Recent work by this group was reported at Geneva, Switzerland, in August, 1955 (7).

SELECTION OF AN EXTRACTING METAL

For the extraction of plutonium from uranium, a metal was required which dissolved plutonium but which was essentially immiscible with uranium. Although uranium phase diagrams were available, a theoretical method was required to predict which metals would dissolve plutonium.

A method due to Hildebrand and Scott (2, p. 333) was used. They deduced as a criterion for the complete miscibility of two liquid metals the expression

$$\tfrac{1}{2}(V_1+V_2)(\delta_1-\delta_2)^2 < 2RT,$$

where V_1 and V_2 are the atomic volumes of metals 1 and 2,

δ_1 and δ_2 are the solubility parameters of 1 and 2,

R is the gas constant and T is the absolute temperature.

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The solubility parameter δ is given by the expression $\delta = (\Delta E_v/V)^{\frac{1}{2}}$ where ΔE_v is the energy of vaporization of the metal. Hildebrand and Scott have calculated the solubility parameters of most metals (2, p. 323). For plutonium a value for δ of 84 at room temperature was determined from the available data.

The miscibility criterion was used to compile a group of metals whose liquids should be miscible with liquid plutonium. From this group were chosen those metals which were immiscible with liquid uranium and which would exist as liquids under one atmosphere pressure in the temperature range 1132° to 1400°C. In this manner silver and the rare earth metals were predicted as possible extracting agents. Of these, silver appeared the most promising because its physical and chemical properties are so markedly different from those of plutonium.

EXPERIMENTAL

Materials and Apparatus

The neutron-irradiated uranium was cut from rods which had been irradiated in the NRX reactor and allowed to decay for three years. For each experiment the uranium was washed immediately before use in dilute nitric acid, water, and then acetone. The silver with a fineness of 999.7 was obtained from the Royal Canadian Mint. Beryllia crucibles were purchased from the Brush Beryllium Co.

Molten uranium and molten silver were contacted in a bell jar type of apparatus which is illustrated in Fig. 1. Cooling water was circulated through a copper coil soldered around the mild steel bell and through a compartment

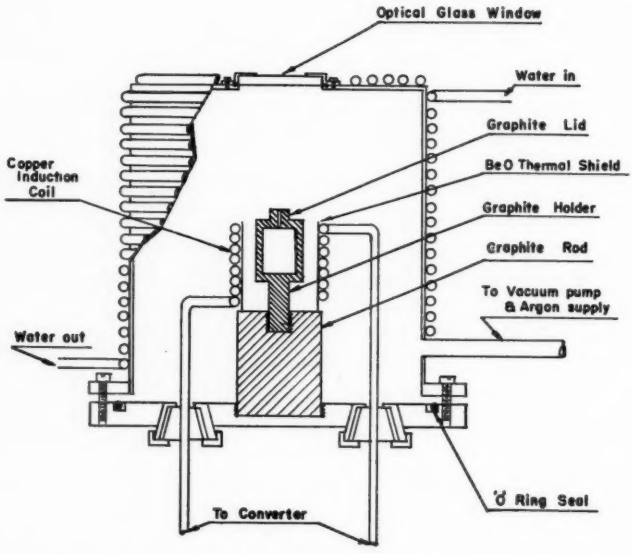

FIG. 1. Diagram of apparatus for contacting uranium and silver.

in the fixed bottom plate. Heat was supplied by a 15 kva. Lepel sparkgap induction furnace. The chamber was evacuated by a Welch Duo-seal mechanical pump and welding grade argon was used as an inert atmosphere. The bell jar resided in a lead-shielded dry box and was viewed through high density glass.

Temperatures were determined with an optical pyrometer. The pyrometer was calibrated from observations of the melting of various solids of known melting point in the apparatus. A rough check of the calibration was obtained by observing the melting point of silver in each run. The temperatures have a probable error of ±25°C.

A different apparatus which will be described in a later communication was used to determine the temperature coefficient of plutonium distribution. The charge was resistance heated and its temperature measured by a thermocouple. The temperatures cited for these measurements are accurate to ±5°C.

Procedures and Analyses

For an experiment weighed amounts of silver and neutron-irradiated uranium in a beryllia crucible were placed in the graphite holder, the bell bolted to the bottom plate, and the chamber evacuated to a pressure of 1 to 10 microns of Hg. The pump was then diverted and the chamber filled to atmospheric pressure with argon. The evacuation and argon filling were repeated three times before heating. The charge was held at temperature for 20 min., which was found to be ample time to establish equilibrium.

After cooling in argon, the metal billet was removed from the crucible and placed in dilute hydrochloric acid to remove the uranium phase. The silver phase which remained was washed thoroughly with water, dried, and weighed. It contained substantially all of the original silver and about 5% by weight of uranium, in approximate agreement with published solubility data (1). This phase was dissolved in dilute nitric acid. In runs in which gold was added, a fluffy black residue, containing most of the gold in the silver layer, remained and was dissolved in aqua regia.

The solutions were analyzed for plutonium by standard radiochemical procedures and the distribution coefficient K_{Pu} calculated where K_{Pu} = mole fraction of plutonium in silver/mole fraction of plutonium in uranium. Gold analyses were performed using the iodide method (5) and K_{Au} calculated from K_{Au} = mole fraction of gold in silver/mole fraction of gold in uranium.

RESULTS AND DISCUSSION

Variation of K_{Pu} with Temperature

The temperature range of interest in this system lies between 1132°C., the melting point of uranium, and 1350°C., above which temperature silver begins to distill at an appreciable rate in one atmosphere of argon. K_{Pu} increases with temperature in this range. The results are summarized in Table I and plotted as log K_{Pu} vs. $1/T$ in Fig. 2.

TABLE I

VARIATION OF K_{Pu} WITH TEMPERATURE
U/Ag weight ratio = 1/1, initial Pu concentration = 0.10±.01%

Run No.	Temp. (°C.)	Wt. U (gm.)	K_{Pu}
B10	1160	3.6345	2.01
B9	1200	4.1647	2.27
B8	1250	3.9676	2.62
B11	1300	3.6350	2.93
B12	1350	3.7455	3.31
B7	1350	4.4005	3.45

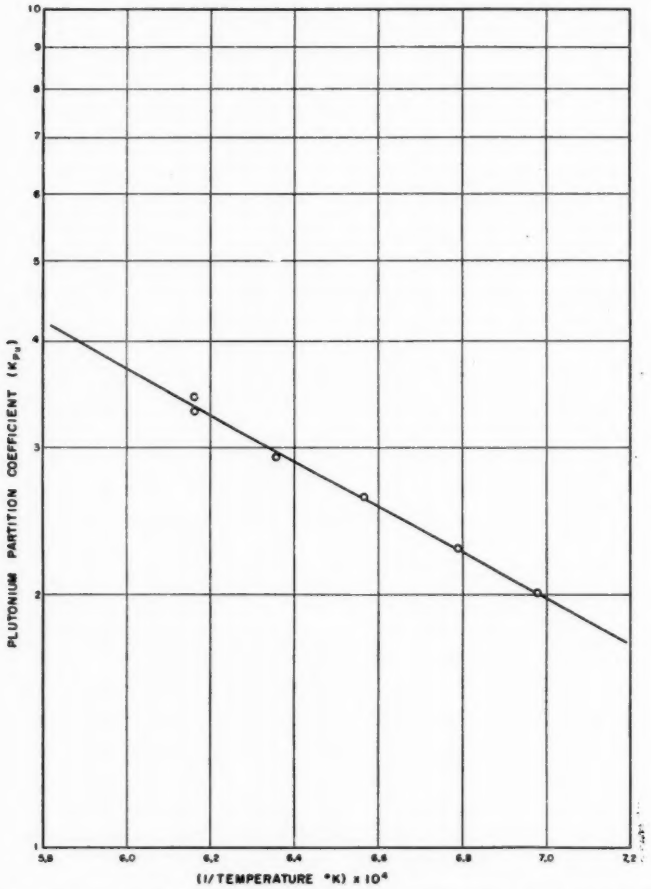

FIG. 2. The variation of K_{Pu} with temperature. U/Ag weight ratio = 1/1. Initial plutonium concentration in uranium = 0.1±0.01%.

The data have been treated by the least squares method to give the equation $\log K_{Pu} = 2.21 - 2.74 \times 10^3/T$. A value for ΔH of 12.5 kcal. is obtained from

the slope of this line. (The uncertainties in a single determination of K_{Pu} are equivalent to an error of ± 0.5 kcal. in ΔH.) This ΔH represents the heat of transfer of one gram-atom of plutonium from liquid uranium to liquid silver and, hence, is the sum of a total or integral heat of solution of plutonium in silver and a heat of dilution of plutonium in neutron-irradiated uranium. From investigations of the volatilization of plutonium from uranium fuel (3, 4) it was concluded that plutonium behaves essentially ideally in molten neutron-irradiated uranium in the temperature range 1540–1770°C. This conclusion implies a zero heat effect associated with the removal of plutonium from this material at such temperatures. Assuming the validity of this conclusion and that ideal behavior extends to the lower temperatures encountered in the present work, the measured heat of transfer is a total heat of solution, per gram-atom of plutonium, of liquid plutonium in liquid silver. Recognizing that the equilibrium concentration of plutonium in silver is about 0.05 atom %, 12.5 kcal. may be considered as $\bar{L}^{\circ}_{Pu}$, the limiting partial molal heat content, relative to liquid plutonium, of plutonium in liquid silver, or "the partial molar heat of mixing of plutonium in silver" (6).

Variation of K_{Pu} with Plutonium Concentration

Plutonium concentrations were varied by choosing uranium of suitable irradiation history and also by adding natural uranium as required. K_{Pu} was found to increase with decreasing plutonium concentration. The data are given in Table II and plotted as log K_{Pu} vs. log(Pu concentration) in Fig. 3. Included in the data is a value for K_{Pu} at 1325°C. and an initial plutonium concentration of 0.1%, calculated from the equation derived in the preceding section.

TABLE II

VARIATION OF K_{Pu} WITH PLUTONIUM CONCENTRATION
U/Ag weight ratio = 1/1, temperature = 1325±25°C.

Run No.	Wt. U (gm.)	Initial Pu conc. in U (%)	K_{Pu}
61	8.823	3.63×10^{-4}	7.48
72	5.852	5.08×10^{-4}	6.87
60	4.631	8.29×10^{-4}	5.93
71	5.642	2.21×10^{-3}	6.58
70	4.113	5.22×10^{-3}	5.16
79	3.847	8.50×10^{-3}	5.31
119	5.408	4.24×10^{-2}	4.20
—	—	1.0×10^{-1}	3.16

The equation log $K_{Pu} = 0.47 - 0.11$ log(initial % Pu in U) describes approximately the increase in plutonium extraction with decreasing plutonium concentration. In the recent work with silver at the Ames laboratory (7) a similar effect was observed in extractions from uranium/chromium alloy but the opposite effect, i.e. a decrease in extraction with decreasing plutonium concentration, was obtained for extractions from uranium. The latter results, which were obtained at 1200 °C. using samples of uranium of two different plutonium concentrations, are also plotted in Fig. 3.

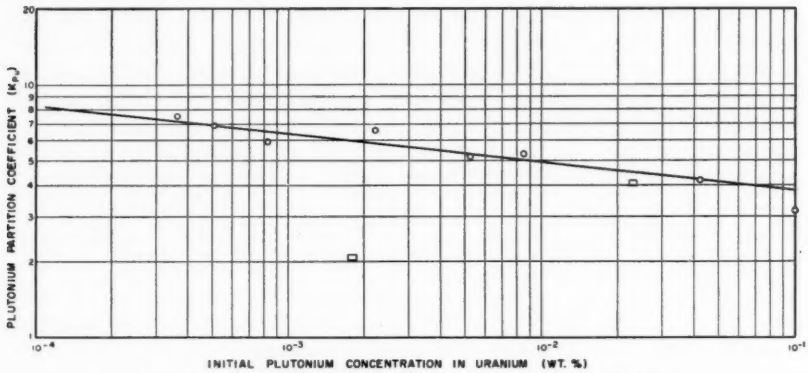

FIG. 3. The variation of K_{Pu} with plutonium concentration.
○ This work. U/Ag weight ratio = 1/1. Temperature 1325±25°C.
□ Voigt's (7) results. U/Ag weight ratio = 1.8/1. Temperature = 1200°C.

Variation of K_{Pu} with the Addition of Gold to the Uranium/Silver System

The effect, on plutonium distribution, of adding other metals to the uranium/silver system was examined for effects analogous to those of complexing or salting-out agents in water/organic solvent systems. The metal was added to a silver and uranium charge and then the melting and contacting operations performed. The metals cerium, tin, gold, copper, magnesium, lead, bismuth, aluminum, lithium, and gallium were considered but all, except gold, showed an adverse effect on plutonium extraction. In each case the weight of the added metal was less than 4% of the weight of uranium in the run.

The extraction of plutonium by silver/gold alloys was studied in greater detail. The extraction exhibits a dependence on gold concentration whereby K_{Pu} passes through a maximum. Also, the distribution of gold between uran-

TABLE III

VARIATION OF K_{Pu} ON THE ADDITION OF GOLD
U/Ag weight ratio = 1/1, initial Pu concentration = 0.01±0.0015%, temperature = 1325±25°C.

Run No.	Wt. U (gm.)	Au added (wt.% of U)	K_{Pu}	K_{Au}*
79	3.847	—	5.31	—
104	4.805	0.69	7.50	—
80	5.170	1.44	5.21	2.56
81	3.984	2.03	4.94	—
82	3.497	2.37	7.54	2.56
83	3.961	2.53	6.31	—
84	4.971	2.91	9.65	2.49
85	5.522	3.23	12.9	2.72
86	4.566	3.75	12.2	2.42
94	4.182	4.02	5.57	—
95	5.528	4.36	7.04	2.26
106	3.688	4.73	4.35	—

**The distribution of gold was not determined for all runs.*

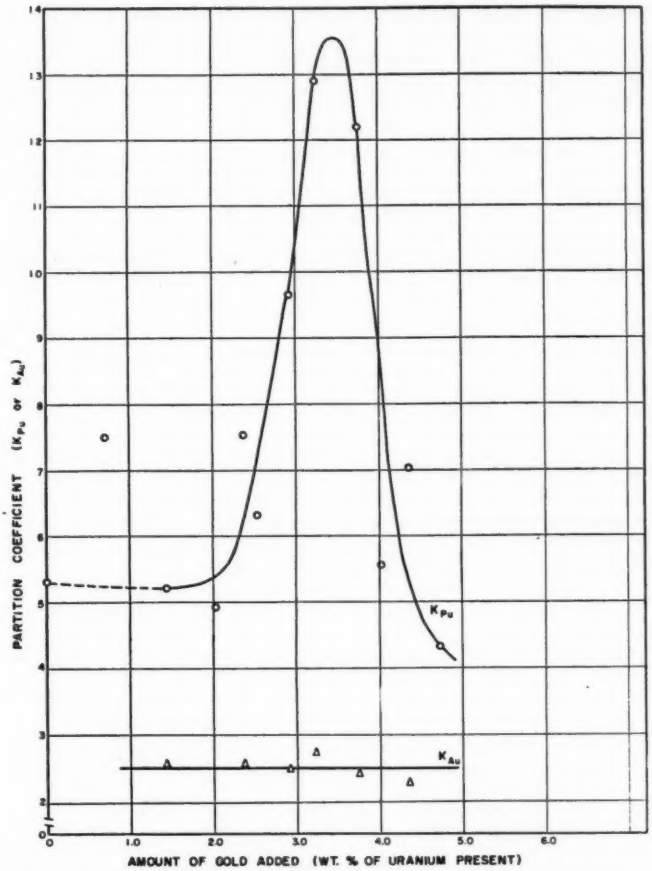

FIG. 4. The variation of K_{Pu} with gold additions. U/Ag weight ratio = 1/1. Temperature = 1325±25°C. Initial plutonium concentration in uranium = 0.01±0.0015%.

ium and silver has been determined and K_{Au}, for a given uranium to silver ratio, appears to be independent of the amount of gold added. A typical set of data is shown in Table III which summarizes the results for a uranium to silver ratio of 1/1. These results are plotted as K_{Pu} vs. Au concentration in Fig. 4. For this ratio a maximum value for K_{Pu} of about 13.5 is obtained, corresponding to a gold addition of 3.5 wt. % of the uranium present.

Similar studies have been made for uranium to silver weight ratios of 2/1, 4/1, and 8/1 at the same temperature (1325°C.) and using uranium of the same initial plutonium concentration (0.01%). The maximum values of K_{Pu} were essentially the same as that found for a 1/1 ratio of uranium to silver. However, maximum plutonium extraction occurs at a different amount of added gold

for each ratio. The gold addition corresponding to maximum K_{Pu} and the average K_{Au} for each ratio are presented in columns 2 and 3 of Table IV. By combining these data, the concentration of gold in silver and in uranium may be calculated for the condition of maximum K_{Pu}. The results of the calculations are shown in columns 5 and 7 of Table IV. It appears that, within the precision of the data, maximum plutonium extraction is achieved at essentially a uniform concentration of gold in silver and also a uniform concentration of gold in uranium independent of the uranium to silver ratio.

TABLE IV

GOLD CONCENTRATIONS IN URANIUM AND IN SILVER FOR MAXIMUM VALUES OF K_{Pu}
Initial Pu concentration = 0.01±0.0015%, temperature = 1325±25°C.

U/Ag ratio (by wt.)	Au addition for max. K_{Pu} (wt.% of U)	K_{Au}	% added Au in U at equil.	Equil. Au conc. in U (wt.%)	% added Au in Ag at equil.	Equil. Au conc. in Ag (wt.%)
1/1	3.5	2.50	15.4	0.5	84.6	3.0
2/1	1.5	1.74	34.1	0.5	65.9	2.0
4/1	1.5	1.77	50.6	0.8	49.4	3.0
8/1	1.0	1.8	66	0.7	34	2.7

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THE PREPARATION AND SOME CLEAVAGE REACTIONS OF ALKYL AND SUBSTITUTED ALKYL METHANESULPHONATES

THE SYNTHESIS OF FLUORIDES, IODIDES, AND THIOCYANATES[1,2]

By F. L. M. Pattison and J. E. Millington

ABSTRACT

Representative esters of methanesulphonic acid were synthesized, and cleaved to form the corresponding fluorides, iodides, and thiocyanates. From this work was developed a convenient laboratory procedure for converting alcohols to fluorides.

The preparation and uses of simple alkyl sulphonates, $ROSO_2R'$, have received considerable attention (7, 8, 9, 10, 26, 27, 30), but little information is available on the reactions of those alkyl sulphonates in which R contains a second functional group. The work described in this paper was undertaken with two objectives: (*a*) to develop a new method of preparing ω-fluoroalkyl compounds, which in turn were required for toxicity studies (20, 21), and (*b*) to examine the reactivity of the sulphonate group relative to that of other functional groups in the same molecule. Methanesulphonates were investigated in most detail, but some benzenesulphonates and *p*-toluenesulphonates were prepared and used for comparison studies on the relative reactivities of the sulphonate moieties.

The sulphonates were prepared by three methods. (1) Esterification of alcohols with the appropriate sulphonyl chloride (19, 26) or fluoride (21) was found to be convenient and economical. Results are summarized in Table I. (2) Occasionally, treatment of iodides or bromides with silver methanesulphonate in acetonitrile (10) proved to be satisfactory, particularly in those instances in which the corresponding hydroxyl compounds were unstable or inaccessible. Results are summarized in Table II. (3) Early in the work, a new method was developed for the preparation of ω-chloroalkyl methanesulphonates by opening of cyclic ethers with methanesulphonyl chloride; an analogous method has subsequently been reported for the preparation of 4-chlorobutyl *p*-toluenesulphonate (11). Conditions and yields are summarized in Table III. One reaction using benzenesulphonyl chloride was carried out: the acid chloride, ethylene oxide, and a trace of zinc chloride were sealed in a glass ampoule and allowed to stand at room temperature for 70 days; 2-chloroethyl benzenesulphonate was obtained in 82% yield.

(1) $ROH + XSO_2R' \rightarrow ROSO_2R' + HX$ (X = F or Cl)

(2) $RX + AgOSO_2R' \rightarrow ROSO_2R' + AgX$ (X = Br or I)

(3) $(CH_2)_nO + MsCl \rightarrow Cl(CH_2)_nOMs$

[1]*Manuscript received January 31, 1956.*
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[2]*To avoid ambiguity, fluorine is not referred to as halogen throughout this report.*
Ms = $CH_3SO_2^-$; *Bs* = $C_6H_5SO_2^-$; *Ts* = p-$CH_3C_6H_4SO_2^-$.

Physical constants of the sulphonates prepared by the above methods are listed in Table IV.

TABLE I

PREPARATION OF METHANE-, BENZENE-, AND *p*-TOLUENE-SULPHONATES FROM ALCOHOLS

Product	Alcohol	Mole	MsCl, mole	MsF, mole	BsCl, mole	TsCl, mole	Base	Mole	Temp., °C.	Time, hr.	Yield, %
$Cl(CH_2)_2OMs$	$Cl(CH_2)_2OH$	1.0		0.22			NaOH	0.22	25	5.5	75
		0.5		0.1			KF	0.3	25	6	88
$Cl(CH_2)_2OBs$		0.94			0.94		C_5H_5N	1.1	−10	5	76
$Cl(CH_2)_2OTs$		1.25				0.5	NaOH	0.5	25	3.5	88
$Cl(CH_2)_3OMs$	$Cl(CH_2)_3OH$	0.75	0.75				C_5H_5N	1.0	− 3	3	83
$Cl(CH_2)_4OMs$	$Cl(CH_2)_4OH$	0.36	0.40				C_5H_5N	1.0	− 5	4	80
$Cl(CH_2)_5OMs$	$Cl(CH_2)_5OH$	0.23	0.24				C_5H_5N	1.0	−15	4	68
		0.21		0.21			NaOH	0.21	−10	4	12
$Br(CH_2)_2OMs$	$Br(CH_2)_2OH$	0.50	0.50				C_5H_5N	0.5	0	2	72
$MeO(CH_2)_2OMs$	$MeO(CH_2)_2OH$	0.30	0.30				C_5H_5N	1.2	0	5	30
$EtO(CH_2)_2OMs$	$EtO(CH_2)_2OH$	0.55	0.50				C_5H_5N	0.7	− 3	2.5	31
$CH_2(CH_2)_2OMs$	$CH_2(CH_2)_2OH$	0.50	0.50				C_5H_5N	0.75	−18	4	89
$CH_2(CH_2)_2OBs$		0.15			0.15		C_5H_5N	0.15	− 5	3.5	64
$CH_2(CH_2)_2OTs$		0.20				0.20	C_5H_5N	0.5	− 5	4	89
$(CH_2)_2CHCH_2OMs$	$(CH_2)_2CHCH_2OH$	0.20	0.20				C_5H_5N	0.63	− 4	3	76
		0.20		0.20			KF	0.30	104	6.5	16
$CH_2{:}CH(CH_2)_2OMs$	$CH_2{:}CH(CH_2)_2OH$	0.50	0.50				C_5H_5N	1.0	− 5	2.5	78.5

TABLE II

PREPARATION OF METHANESULPHONATES FROM HALIDES

Product	Halide	Mole	Silver methanesulphonate, mole	Yield, %
$MsOCH_2COOEt$	ICH_2COOEt	0.1	0.1	62
$MsOCH_2COCH_3$	$BrCH_2COCH_3$	0.2	0.2	43.5
$MsOCH_2CH{:}CHCOOEt$	$BrCH_2CH{:}CHCOOEt$	0.3	0.3	60
$MsOCH(COOEt)_2$	$BrCH(COOEt)_2$	0.1	0.1	47
$MsOCH_2CH(OEt)_2$	$BrCH_2CH(OEt)_2$	0.1	0.1	60

TABLE III

CONVERSION OF CYCLIC ETHERS TO ω-CHLOROALKYL METHANESULPHONATES

Cyclic ether	Moles	MsCl, mole	Temp., °C.	Time, hr.	Conversion, %	Yield, %
$(CH_2)_2O$	2.0	0.50	25	180	33	47
	1.5	0.51	40	32	35	50
	0.5	0.23	22	1680	22	46
$(CH_2)_4O$	0.33	0.33	80	4	26	69
	0.33	0.33	85	20	36	53

Reactions of Sulphonates with Potassium Fluoride (*8, 21*)

$$ROMs + KF \rightarrow RF + MsOK$$

Initially, replacement of the sulphonoxy group (CH_3SO_2O–) by fluoride was attempted in methanol; however, the isolation of a relatively large proportion

TABLE IV

PHYSICAL CONSTANTS OF METHANE-, BENZENE-, AND *p*-TOLUENE-SULPHONATES

Compound	Boiling point		n_D^{25}	d_4^{20}
	°C.	mm.		
2-Chloroethyl methanesulphonate	130	11.5	1.4545	1.420
3-Chloropropyl methanesulphonate	143–146	9	1.4548	1.337
4-Chlorobutyl methanesulphonate	115	0.5	1.4570	1.272
5-Chloroamyl methanesulphonate	128	1	1.4581	1.236
2-Bromoethyl methanesulphonate	140–142	11	1.4805	1.703
2-Methoxyethyl methanesulphonate[a]	126	12	1.4308	
2-Ethoxyethyl methanesulphonate[b]	132–134	12	1.4303	
n-Hexyl methanesulphonate[c]	107–108	3.5	1.4324	
Isobutyl methanesulphonate[d]	99–101	11.5	1.4232	
Pent-4-enyl methanesulphonate	79–80	0.15	1.4444	1.123
Ethyl methanesulphonoxyacetate	148	9	1.4365	1.317
Methanesulphonoxyacetone	104	0.4	1.4445	1.305
Ethyl 4-methanesulphonoxycrotonate	120	0.2	1.4628	1.250
Diethyl methanesulphonoxymalonate	117	0.1	1.4400	1.292
Diethyl methanesulphonoxyacetal	82	0.15	1.4338	1.183
2-Chloroethyl benzenesulphonate[e]	139	2	1.5276	
n-Hexyl benzenesulphonate[f]	125	0.2	1.4952	
2-Chloroethyl *p*-toluenesulphonate[g]	142	1	1.5282	
n-Hexyl *p*-toluenesulphonate[h]	145	0.5	1.4968	

[a] *Chapman and Owen (4) report b.p. 80° at 0.4 mm. and* n_D^{20} *1.4314.*

[b] *Newman and Magerlein (19) report b.p. 122–124° at 7 mm. and* n_D^{25} *1.4303.*

[c] *Williams and Mosher (30) report b.p. 78° at 1 mm. and* n_D^{20} *1.4336.*

[d] *Williams and Mosher (30) report b.p. 53° at 1 mm. and* n_D^{20} *1.4245.*

[e] *Bert (2) reports b.p. 192° at 15 mm.*

[f] *Emling (9) reports b.p. 135–136° at 0.5 mm. and* n_D^{25} *1.4952.*

[g] *Tipson and Cretcher (29) report b.p. 140° at 1.5 mm. and* n_D^{25} *1.5280.*

[h] *Drahowzal and Klamann (7) report b.p. 149° et 0.5 mm. and* n_D^{20} *1.4996.*

of hexyl methyl ether from a mixture of potassium fluoride and hexyl methanesulphonate indicated the unfavorable properties of this solvent. Dimethyl formamide, dimethyl sulphoxide, and diethyl cellosolve were found to be unsuitable. Ethylene glycol gave results analogous to those obtained with methanol, but diethylene, triethylene, and tetraethylene glycols did not exhibit the same tendency for ether formation. Diethylene glycol was finally selected as the solvent for this study because of its availability and ease of purification. The product was continuously removed as the reaction proceeded. Conditions and yields are summarized in Table V.

The main side reactions were: (*a*) dehydration of diethylene glycol in the presence of potassium fluoride to give dioxane; and (*b*) replacement of halide by fluoride to give ω,ω′-difluoroalkanes. In all the cleavage reactions, appreciable quantities of dioxane were formed, and when temperatures higher than those listed in Table V were used, difluoroalkanes were obtained from ω-haloalkyl methanesulphonates in 40–60% yield.

TABLE V

PREPARATION OF ALKYL AND SUBSTITUTED ALKYL FLUORIDES
(Molar scale: 0.1 mole methanesulphonate; 0.2–0.3 mole potassium fluoride; *ca.* 200 gm. solvent)

Product	Methanesulphonate	Solvent[a]	Time, hr.	Temp., °C.	Press., mm.	Yield, %
$CH_3(CH_2)_5F$	$CH_3(CH_2)_5OMs$	MeOH	17	66	750	9
		MeOH	17	95	—	0
		E.G.	4	100	300	10
		D.G.	9	105	750	18
		D.G.	4	100	300	67
		Tri E.G.	4	100	300	52[b]
		Tetra E.G.	4	100	300	50[b]
		D.G.	4	100	300	50[b]
$Cl(CH_2)_2F$	$Cl(CH_2)_2OMs$	MeOH	11.5	66	740	49
		D.G.	4.5	100	300	73
$Cl(CH_2)_3F$	$Cl(CH_2)_3OMs$	D.G.	4	100	320	65
$Cl(CH_2)_4F$	$Cl(CH_2)_4OMs$	D.G.	4.5	100	220	64
$Cl(CH_2)_5F$	$Cl(CH_2)_5OMs$	D.G.	4.5	100	70	66
$Br(CH_2)_2F$	$Br(CH_2)_2OMs$	D.G.	4.5	125	280	20
		D.G.	4	100	300	67
$MeO(CH_2)_2F$	$MeO(CH_2)_2OMs$	D.G.	4	100	300	75
$EtO(CH_2)_2F$	$EtO(CH_2)_2OMs$	D.G.	4	100	300	68
$CH_2{:}CH(CH_2)_2F$	$CH_2{:}CH(CH_2)_2OMs$	D.G.	2.2	100	450	36.5
FCH_2COOEt	$MsOCH_2COOEt$	D.G.	2	100	340	47
FCH_2COCH_3	$MsOCH_2COCH_3$	D.G.	1.5	100	320	50
$FCH_2CH{:}CHCOOEt$	$MsOCH_2CH{:}CHCOOEt$	D.G.	3	100	13	50
$FCH(COOEt)_2$	$MsOCH(COOEt)_2$	D.G.	3.5	100	17	0
$FCH_2CH(OEt)_2$	$MsOCH_2CH(OEt)_2$	D.G.	2.5	100	75	0

[a]*E.G. = Ethylene glycol. D.G. = Diethylene glycol. Tri E.G. = Triethylene glycol. Tetra E.G. = Tetraethylene glycol.*
[b]*Carried out using 0.05 mole of methanesulphonate.*

A number of reactions were carried out by the same procedure and under the same conditions as described above, in order to determine the relative reactivities of the sulphonate moieties. The results, shown in Table VI, do not exhibit any characteristic trend.

TABLE VI

INFLUENCE OF THE SULPHONATE MOIETY
(Molar scale: 0.1 mole sulphonate; 0.2–0.3 mole potassium fluoride; *ca.* 200 gm. solvent)

Product	Sulphonate	Solvent	Temp., °C.	Press., mm.	Yield, %
$Cl(CH_2)_2F$	$Cl(CH_2)_2OMs$	MeOH	66	740	49
	$Cl(CH_2)_2OBs$	MeOH	66	740	60
	$Cl(CH_2)_2OTs$	MeOH	66	740	0
		MeOH	95	—	25
	$Cl(CH_2)_2OMs$	D.G.	100	300	73
	$Cl(CH_2)_2OBs$	D.G.	100	300	77
	$Cl(CH_2)_2OTs$	D.G.	100	300	76
$CH_3(CH_2)_5F$	$CH_3(CH_2)_5OMs$	D.G.	100	300	67
	$CH_3(CH_2)_5OBs$	D.G.	100	300	55
	$CH_3(CH_2)_5OTs$	D.G.	100	300	58

Attempts were then made to combine the two stages—esterification and cleavage—in order to devise a continuous one-step process for conversion of hydroxyl to fluoride. For satisfactory yields in the potassium fluoride cleavage, it is advantageous to exclude all traces of sulphonyl chlorides and of ionic chloride, the latter competing with the fluoride during the cleavage. Consequently a modified preparation of sulphonates was developed in this laboratory[3](21); this involved treatment of the alcohol with a sulphonyl fluoride, in the presence of an excess of anhydrous potassium fluoride to remove the liberated hydrogen fluoride as potassium bifluoride:

$$X(CH_2)_nOH + MsF + KF \rightarrow X(CH_2)_nOMs + KFHF.$$

The cleavage of the resultant sulphonate was then effected by the excess potassium fluoride. The over-all reaction may be represented thus:

$$X(CH_2)_nOH + MsF + 2KF \rightarrow X(CH_2)_nF + MsOK + KFHF.$$

A limited number of alcohols were converted to the corresponding fluorides by this method; yields are shown in Table VII. When applied to unsubstituted alcohols this method failed at the esterification stage. From the gradation in yields obtained (Table VII: $Cl(CH_2)_2- > Cl(CH_2)_3- > Cl(CH_2)_5-$; Cl– > Br–; Cl– > MeO– > EtO–), it seems probable that a fundamental requirement is the presence in the alcohol of an electronegative group capable of exerting an inductive effect; hence the method is of very limited applicability.

TABLE VII

CONVERSION OF ALCOHOL TO FLUORIDE BY CONTINUOUS METHOD

Alcohol	Yield of fluoride, %
$Cl(CH_2)_2OH$	53[a]
	60[b]
$Cl(CH_2)_3OH$	10[a]
$Cl(CH_2)_5OH$	0[a]
$Br(CH_2)_2OH$	35[a]
$MeO(CH_2)_2OH$	43[a]
$EtO(CH_2)_2OH$	27[a]
	29[b]

[a] *Via methanesulphonate.*
[b] *Via benzenesulphonate.*

To circumvent this difficulty, a semicontinuous method was examined. Adapted from the previously reported procedure of Edgell and Parts (8), this involved the preparation of the sulphonate using the appropriate sulphonyl chloride, followed by isolation and azeotropic drying, but not purification; cleavage with potassium fluoride was then effected in the usual way. Results are summarized in Table VIII. This method affords a convenient and simple means of converting alcohols to the corresponding fluorides.

[3] *Originally developed by S. B. D. Hunt.*

TABLE VIII

CONVERSION OF ALCOHOL TO FLUORIDE BY "SEMICONTINUOUS" METHOD

Alcohol	Sulphonate intermediate	Yield of fluoride, %
$CH_3(CH_2)_5OH$	$CH_3(CH_2)_5OMs$	54
	$CH_3(CH_2)_5OBs$	54
	$CH_3(CH_2)_5OTs$	47
$CH_3(CH_2)_9OH$	$CH_3(CH_2)_9OMs$	48
	$CH_3(CH_2)_9OBs$	35

Physical constants of the fluorides prepared by the above methods are listed in Table IX.

TABLE IX

PHYSICAL CONSTANTS OF FLUORIDES

Compound	Boiling point		n_D^{25}
	°C.	mm.	
2-Fluoroethyl chloride[a]	52.5	745	1.3742
3-Fluoropropyl chloride[b]	79.5	740	1.3863
4-Fluorobutyl chloride[c]	114.5	740	1.4020
5-Fluoroamyl chloride[d]	74	76	1.4110
2-Fluoroethyl bromide[e]	73–74	750	1.4240
2-Fluoroethyl methyl ether[f]	56–57	735	1.3458
2-Fluoroethyl ethyl ether[g]	72	740	1.3582
n-Hexyl fluoride[h]	91–92	745	1.3732
n-Decyl fluoride[i]	74–75	13	1.4080
Pent-4-enyl fluoride[j]	59	735	1.3746
Ethyl fluoroacetate[k]	115–117	740	1.3750
Fluoroacetone[l]	72.5–73	740	1.3650
Ethyl 4-fluorocrotonate	53.5–54	11	1.4180

[a]*Razumovskii and Fridenberg (23) report b.p. 52–53° and* n_D^{20} *1.3775.*

[b]*Hoffmann (16) reports b.p. 82.1° and* $n_D^{27.2}$ *1.3855.*

[c]*Hoffmann (15) reports b.p. 114.7° and* n_D^{23} *1.4025.*

[d]*Hoffmann (15) reports b.p. 143.2° and* n_D^{23} *1.4120.*

[e]*Hoffmann (16) reports b.p. 71–72°.*

[f]*Schrader (25) reports b.p. 59–60° at 760 mm.*

[g]*Gryszkiewicz-Trochimowski et al. (12) report b.p. 74.5–75.5°.*

[h]*Desreux (6) reports b.p. 93.15° at 755 mm. and* n_D^{20} *1.3748.*

[i]*Swarts (28) reports b.p. 183.5°.*

[j]*Hoffmann (15) reports b.p. 61.9–62.1° at 760 mm.*

[k]*Redemann et al. (24) report b.p. 114–118° and* n_D^{21} *1.3759.*

[l]*Ray et al. (22) report b.p. 72°.*

Reactions of Chloroalkyl Sulphonates with Sodium Iodide

$$Cl(CH_2)_nOMs + NaI \rightarrow Cl(CH_2)_nI + MsONa$$

The preparations listed in Table X were studied for various reasons: (*a*) to obtain samples of the chloroiodides for other work; (*b*) to devise an improved procedure for preparing 2-chloroethyl iodide, which is inconvenient to obtain

by other means; (*c*) to compare the procedure with the well-known half-iodination of dichloroalkanes; and (*d*) to obtain information regarding the relative reactivities of the chloride and sulphonoxy groupings in a typical S_N2 reaction.

The chloroalkyl sulphonates were allowed to react at room temperature with an equimolar quantity of sodium iodide in acetone. Yields of the corresponding chloroalkyl iodides are shown in Table X. It can be seen that the reaction is as efficient as the half-iodination procedure for which yields of 50–70% are reported (1, 13), and that 2-chloroethyl iodide can be obtained in satisfactory yield. The sulphonoxy grouping is preferentially replaced under the conditions employed.

TABLE X

PREPARATION AND PHYSICAL PROPERTIES OF CHLOROALKYL IODIDES

Compound	Yield, %	Boiling point		n_D^{25}
		°C.	mm.	
2-Chloroethyl iodide[a]	16[b]	30	12.5	
	49[c]	32–33	13	1.5615
3-Chloropropyl iodide[d]	70	58–59	13	1.5462
4-Chlorobutyl iodide[e]	59	82	10	1.5398

[a] *Meyer and Wurster (18) report b.p. 137–138°.*
[b] *From 2-chloroethyl methanesulphonate.*
[c] *From 2-chloroethyl benzenesulphonate.*
[d] *Hass and Huffman (13) report b.p. 60° at 15 mm.*
[e] *Field and Holsten (11) report b.p. 94° at 17 mm. and* n_D^{25} *1.5382.*

Reactions of Chloroalkyl Methanesulphonates with Potassium Thiocyanate

$$Cl(CH_2)_nOMs + KSCN \rightarrow Cl(CH_2)_nSCN + MsOK$$

To confirm the preferential replacement of the sulphonoxy grouping referred to above, the chloroalkyl methanesulphonates were treated with equimolar quantities of potassium thiocyanate in boiling aqueous ethanol (80%). Results and constants of the chloroalkyl thiocyanates are shown in Table XI.

TABLE XI

PREPARATION AND PHYSICAL CONSTANTS OF CHLOROALKYL THIOCYANATES

Compound	Yield, %	Boiling point		n_D^{25}
		°C.	mm.	
2-Chloroethyl thiocyanate[a,b]	69	93	14	1.5102
3-Chloropropyl thiocyanate[c]	62	115	12	1.5024
4-Chlorobutyl thiocyanate	67	134	12	1.4989
5-Chloroamyl thiocyanate	66	144–145	10	1.4950
n-Hexyl thiocyanate[d]	80	108–109	18	1.4627

[a] *Delepine and Ville (5) report b.p. 106° at 25 mm.*
[b] *Ethylene dithiocyanate,* $NCS(CH_2)_2SCN$, *was also isolated (14%), recrystallized from ethanol, m.p. 89–90°; Kaufmann and Oehring (17) report m.p. 90°.*
[c] *Henry (14) reports b.p. 222–223°.*
[d] *Cahours and Pelouze (3) report b.p. 215–220°.*

EXPERIMENTAL[4]

TABLE XII

ANALYTICAL DATA FOR NEW COMPOUNDS

	C, %		H, %		Hal., %	
	Calc.	Found	Calc.	Found	Calc.	Found
$Cl(CH_2)_2OMs$	22.70	22.66	4.45	4.46	22.35	22.15
$Cl(CH_2)_3OMs$	27.83	27.88	5.25	5.21		
$Cl(CH_2)_4OMs$	32.18	32.12	5.94	5.75	18.99	18.95
$Cl(CH_2)_5OMs$	35.91	36.06	6.53	6.28	17.67	17.55
$Br(CH_2)_3OMs$	17.74	17.42	3.47	3.30	39.35	39.15
$CH_2{:}CH(CH_2)_3OMs$	43.90	43.69	7.32	7.43		
$MsOCH_2COOEt$	32.97	33.21	5.49	5.45		
$MsOCH_2COCH_3$	31.58	31.53	5.26	5.36		
$MsOCH_2CH{:}CHCOOEt$	40.38	40.49	5.77	5.97		
$MsOCH(COOEt)_2$	37.86	38.02	5.55	5.39		
$MsOCH_2CH(OEt)_2$	39.62	39.44	7.55	7.55		
$FCH_2CH{:}CHCOOEt$	54.54	54.44	6.82	6.66		
$Cl(CH_2)_4SCN$	40.14	40.27	5.35	5.36	23.74	23.59
$Cl(CH_2)_5SCN$	44.03	44.13	6.12	6.08	21.71	21.61

Preparation of Methanesulphonates

The following are representative examples of the procedures employed in the preparation of methanesulphonates.

Method (1). The reaction of an Alcohol with a Sulphonyl Halide

2-Chloroethyl methanesulphonate

A mixture of 2-chloroethanol (80.5 gm., 1.0 mole) and methanesulphonyl fluoride (21.7 gm., 0.22 mole) was stirred at −15°, and powdered sodium hydroxide (8.8 gm., 0.22 mole) was added in small portions. Stirring was continued at 25° for five and one-half hours. The product was diluted with water and extracted with ether. The extracts were washed with water and dried over anhydrous sodium sulphate. The ether was removed and fractionation of the residue gave 2-chloroethyl methanesulphonate (26.2 gm., 75%).

2-Chloroethyl methanesulphonate

A mixture of 2-chloroethanol (40.5 gm., 0.5 mole), methanesulphonyl fluoride (9.8 gm., 0.1 mole), and anhydrous potassium fluoride (17.4 gm., 0.3 mole) was vigorously stirred at room temperature for six hours and then allowed to stand overnight. It was diluted with water and extracted with ether. The extract was dried over anhydrous sodium sulphate, the ether removed, and the residue fractionated to give 2-chloroethyl methanesulphonate (14 gm., 88%).

3-Chloropropyl methanesulphonate

A mixture of 3-chloropropanol (71 gm., 0.75 mole) and pyridine (79 gm., 1.0 mole) was stirred in a flask cooled in an ice–salt bath, and methanesulphonyl chloride (86 gm., 0.75 mole) was added slowly over a period of one

[4]*The microanalyses were performed by Mr. J. F. Alicino, Metuchen, N.J. Results are shown in Table XII.*
Boiling points are uncorrected.
Physical constants are listed in the appropriate tables.

and one-half hours. Stirring was continued for a further three hours. The reaction product was diluted with water and 6 *N* hydrochloric acid until there was no pyridine odor, and then extracted with ether. The extracts were washed successively with water, aqueous sodium carbonate, and water again. After drying over anhydrous calcium chloride and removal of the ether, fractionation of the residue gave 3-chloropropyl methanesulphonate (106.5 gm., 83%).

Method (2). The Reaction of a Halide with Silver Methanesulphonate

Ethyl 4-methanesulphonoxycrotonate

A mixture of ethyl 4-bromocrotonate (58 gm., 0.3 mole), silver methanesulphonate (61 gm., 0.3 mole), and acetonitrile (200 ml.) was heated under reflux on a water bath for one hour. After cooling, the precipitated silver bromide was removed by filtration and the filtrate concentrated. After a further amount of precipitate had been removed, the filtrate was taken up in ether, washed successively with water, aqueous sodium carbonate, and water again, and dried over anhydrous sodium sulphate. After removal of the ether, fractionation of the residue gave ethyl 4-methanesulphonoxycrotonate (37.3 gm., 60%).

Method (3). The Reaction of a Cyclic Ether with a Sulphonyl Halide

2-Chloroethyl methanesulphonate

Ethylene oxide (66 gm., 1.5 moles), methanesulphonyl chloride (58 gm., 0.51 mole), freshly fused zinc chloride (2 gm.), and ether (100 ml.) were placed in a stainless steel bomb, and heated at 40° for 32 hr. with constant agitation. On cooling, the solid material was removed by filtration, and the filtrate fractionated to give methanesulphonyl chloride (23.2 gm.) of b.p. 52° at 12 mm., and 2-chloroethyl methanesulphonate (27.8 gm.). This represents a yield of 50% based on reacted starting material.

2-Chloroethyl benzenesulphonate

A mixture of ethylene oxide (21 gm., 0.48 mole), benzenesulphonyl chloride (26.5 gm., 0.15 mole), and zinc chloride (0.5 gm.) was sealed in a glass ampoule and allowed to stand at room temperature (*ca.* 22°) for 70 days. The mixture was filtered to remove solid material, and the filtrate on fractionation yielded 2-chloroethyl benzenesulphonate (27 gm., 82%).

4-Chlorobutyl methanesulphonate

Tetrahydrofuran (24.6 gm., 0.33 mole), methanesulphonyl chloride (39 gm., 0.33 mole), anhydrous zinc chloride (1.0 gm.), and ether (100 ml.) were heated in a stainless steel bomb at 80° with constant agitation for four hours. On cooling, the product was filtered to remove solid material, and the filtrate fractionated to give methanesulphonyl chloride (25 gm.) of b.p. 52° at 12 mm., and 4-chlorobutyl methanesulphonate (15.7 gm.). This represents a yield of 69% based on reacted starting material.

Preparation of Fluorides

The following procedures illustrate the methods employed for the preparation of fluorides.

2-Fluoroethyl Chloride

A mixture of 2-chloroethyl methanesulphonate (15.9 gm., 0.1 mole), potassium fluoride (11.6 gm., 0.2 mole), and methanol (200 ml.) was heated under reflux with intermittent stirring for 11½ hr. On cooling, it was diluted with water and extracted with di-*n*-butyl ether. The extracts were dried over anhydrous sodium sulphate and on fractionation gave 2-fluoroethyl chloride (4 gm., 49%).

3-Fluoropropyl Chloride

A mixture of 3-chloropropyl methanesulphonate (17.3 gm., 0.1 mole), anhydrous potassium fluoride (11.6 gm., 0.2 mole), and diethylene glycol (200 gm.) was placed in a three-necked flask equipped with a thermometer, precision-bore stirrer, and a short still head carrying a condenser and ice-cooled receiver. The stirrer was started, the pressure in the system reduced to 320 mm., and the temperature maintained at 100°. The distillate was collected over a period of four hours, and on fractionation gave 3-fluoropropyl chloride (6.3 gm., 65%).

Ethyl 4-Fluorocrotonate

A mixture of ethyl 4-methanesulphonoxycrotonate (21 gm., 0.1 mole), anhydrous potassium fluoride (11.6 gm., 0.2 mole), and diethylene glycol (200 gm.) was placed in a flask fitted with a thermometer, precision-bore stirrer, and a still head carrying a condenser and ice-cooled receiver. The flask was heated to 100°, and the distillate was collected at a pressure of 13 mm. over a period of three hours. This was dissolved in ether, washed with water, and dried over anhydrous sodium sulphate. After removal of the ether, the residue on fractionation through a modified Podbielniak column gave ethyl 4-fluorocrotonate (6.6 gm., 50%).

2-Fluoroethyl Chloride (Continuous Method)

In the equipment described above, a mixture of 2-chloroethanol (24.1 gm., 0.3 mole), methanesulphonyl fluoride (29.4 gm., 0.3 mole), and anhydrous potassium fluoride (34.8 gm., 0.6 mole) was stirred at room temperature for 24 hr. Diethylene glycol (250 gm.) and anhydrous potassium fluoride (11.6 gm., 0.2 mole) were added, the pressure in the system was reduced to 300 mm., and the temperature raised to 100°. The distillate (16.6 gm.), collected over four hours, gave on fractionation 2-fluoroethyl chloride (13.1 gm., 53%).

n-Hexyl Fluoride (Semicontinuous Method)

n-Hexyl alcohol (15.3 gm., 0.15 mole) and pyridine (30 gm., 0.38 mole) were stirred at −15°, and to the mixture methanesulphonyl chloride (17.1 gm., 0.15 mole) was slowly added. The mixture was stirred for a further four hours and diluted with water and 6 *N* hydrochloric acid until there was no pyridine odor. The aqueous layer was extracted with methylene chloride, and the combined organic layer and extracts were washed with water. These were then transferred to the three-necked flask described above. The water – methylene chloride azeotrope was distilled, and any residual low-boiling material removed under aspirator pressure. Diethylene glycol (250 gm.) and anhydrous

potassium fluoride (17.4 gm., 0.3 mole) were added, the temperature was raised to 100°, and the distillate collected over one and one-half hours at a pressure of 300 mm. Fractionation of this yielded *n*-hexyl fluoride (8.8 gm., 54%).

Preparation of Chloroalkyl Iodides

The preparation of 3-chloropropyl iodide is representative.

3-Chloropropyl Iodide

A mixture of 3-chloropropyl methanesulphonate (17.3 gm., 0.1 mole), sodium iodide (15.0 gm., 0.1 mole), and anhydrous acetone (100 ml.) was allowed to stand at room temperature, with occasional shaking, for 72 hr. It was diluted with water and extracted with ether. The extracts were washed successively with aqueous sodium thiosulphate and with water, and dried over anhydrous sodium sulphate. Removal of the ether and fractionation of the residue gave 3-chloropropyl iodide (10.5 gm.) and 3-chloropropyl methanesulphonate (4.5 gm.). This represents a yield of 70% based on reacted starting material.

Preparation of Chloroalkyl Thiocyanates

The preparation of 3-chloropropyl thiocyanate is representative.

3-Chloropropyl Thiocyanate

A mixture of 3-chloropropyl methanesulphonate (17.3 gm., 0.1 mole), potassium thiocyanate (9.7 gm., 0.1 mole), and 80% ethanol (25 ml.) was heated under reflux on a water bath for 16 hr. The mixture was diluted with water and extracted with ether. The extract was dried over anhydrous sodium sulphate and fractionated, yielding 3-chloropropyl thiocyanate (10 gm., 62%).

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THE ADSORPTION OF NITROGEN BY CARBON BLACK AND GRAPHITE[1]

By H. L. McDermot and B. E. Lawton

ABSTRACT

The adsorption of nitrogen by a carbon black designated as Spheron 9 has been measured at 78°K. and 71°K. The second type of hysteresis previously reported for three Acheson graphites has also been observed for the adsorption of nitrogen by Spheron 9 at both temperatures. Unlike the graphite isotherms, it was possible to scan the hysteresis loop of the Spheron isotherm. The adsorption of nitrogen has been measured for an artificial graphite in which the ash had been leached out by treatment with hydrofluoric acid. The results were compared with those obtained previously for a sample of the unleached graphite. It was found that although the surface area was altered by this treatment, the hysteresis effects remained unchanged.

INTRODUCTION

In an earlier communication (3), two hysteresis effects were reported for the adsorption of nitrogen, oxygen, and argon on three Acheson graphites at liquid nitrogen temperatures. The first of these was attributed to the porous structure of the graphite and the second to swelling of the graphite crystallites. The second type of hysteresis took the form of an initial isotherm which lay below subsequent isotherms. Except for the region of the isotherm which exhibited "pore" hysteresis, the isotherms after the first were observed to be reversible provided the sample was not fully desorbed. The upper or reversible isotherm could only be reached after a certain relative pressure had been exceeded. At relative pressures below this value, the initial isotherm was observed to be reversible, or very nearly so. By analogy with known cases of swelling hysteresis, it was postulated that this second type of hysteresis was caused by intercrystalline swelling. In the course of the work with these graphites it was found necessary for purposes of comparison to introduce an isotherm for a non-porous carbon. The adsorption isotherm of nitrogen on a non-porous carbon black (Spheron 9) was chosen. More detailed measurements on this system since publication of the earlier paper have revealed hysteresis effects similar to the second type of hysteresis observed with the graphite systems. The new work presented here includes scanning runs and an isotherm at another temperature.

In the work referred to above (3), the adsorption of gases was studied on three Acheson graphites which were used as they were received from the manufacturers. One of these graphites, which was designated by the symbol G-3, was selected for a study of the effect of ash removal. This graphite was chosen because it had a high ash content and displayed "swelling" hysteresis to the greatest extent. It will be shown that although removal of the ash displaces the isotherm downwards, it does not alter the amount of hysteresis.

EXPERIMENTAL AND RESULTS

The carbon black employed in these studies was a non-porous material

[1]*Manuscript received February 9, 1956.*
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designated as Spheron 9. It was supplied to us by the Godfrey L. Cabot Co., Cambridge, Mass.

The graphite used was a sample of G-3 in which the ash content was reduced from 0.77% to 0.09% by leaching with hydrofluoric acid. This ash-free graphite will be designated as GF-3.

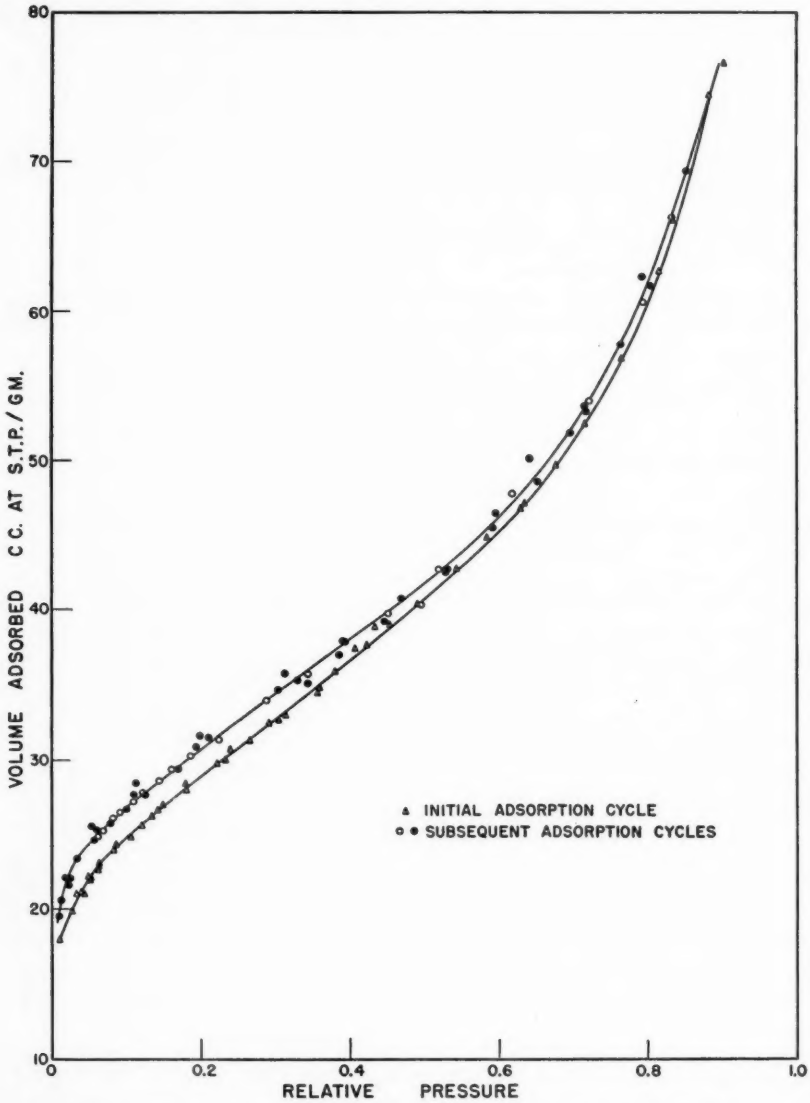

FIG. 1. Isotherm of nitrogen adsorbed by Spheron 9 at 78°K. Desorption points from the initial adsorption cycle and from subsequent cycles are represented by inked-in circles.

Nitrogen was supplied by the Canadian Liquid Air Co. It was stated to be 99.5% nitrogen and was used without further purification.

The apparatus and procedure was exactly as described previously (3).

The adsorption isotherm of nitrogen on Spheron 9 at 78°K. is shown in Fig. 1. The triangles represent the initial adsorption curve after outgassing. The circles represent the first desorption curve as well as points taken on subsequent adsorption cycles. It will be noted that the upper curve is reversible. Scanning runs were made in which desorption was first carried out from a relative pressure of 0.356 followed by readsorption from $p/p_0 = 0.039$ to $p/p_0 = 0.514$. Desorption from this latter pressure resulted in a curve which was well within the hysteresis loop. The scanning curves along with a desorption curve from a high relative pressure are displayed in Fig. 2. In contrast

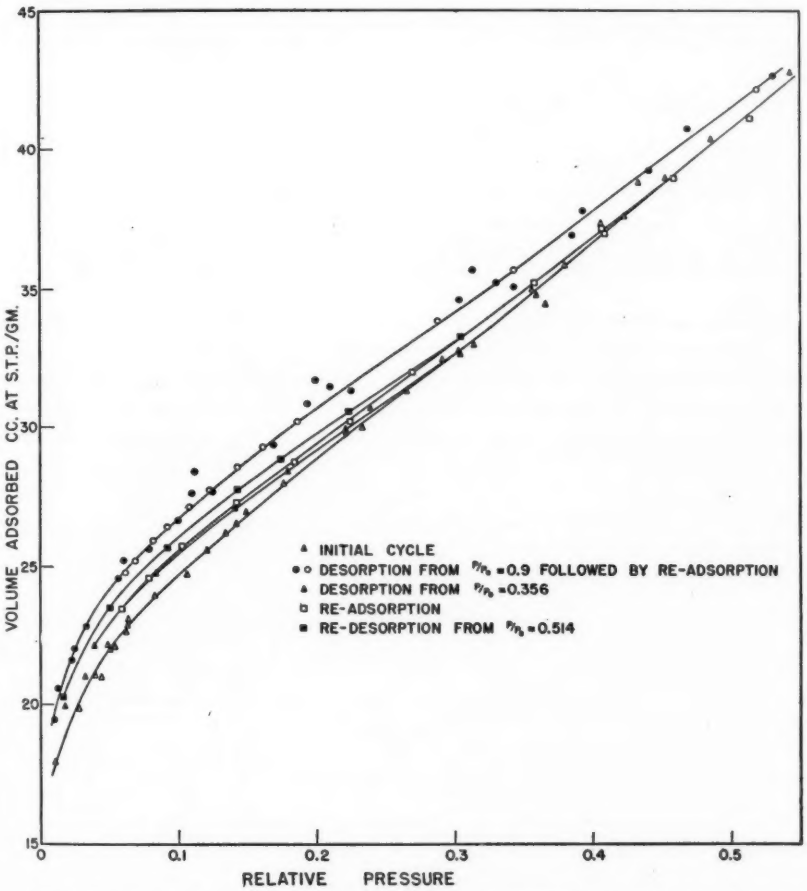

FIG. 2. Isotherm of nitrogen adsorbed by Spheron 9 at 78°K. showing the scanning runs. Desorption points are represented by inked-in symbols.

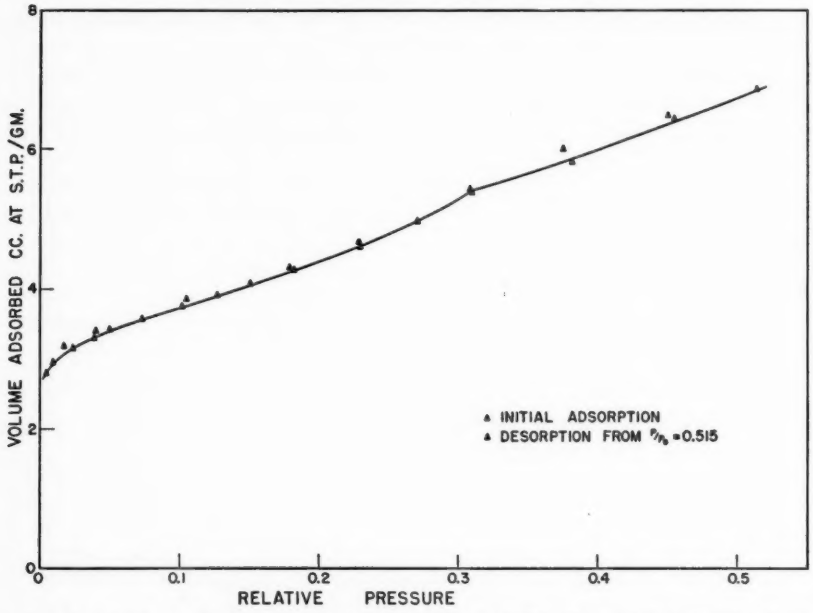

FIG. 3. Isotherm of nitrogen adsorbed by GF-3 at 71°K. illustrating desorption from moderate relative pressures. Desorption points are represented by inked-in triangles.

to the case of Spheron 9, the initial curve for graphite is very nearly reversible at moderate relative pressures. For example the isotherm shown in Fig. 3 for the adsorption of nitrogen on GF-3 at 71°K. exhibits only slight hysteresis. The adsorption of nitrogen by Spheron 9 was also measured at 71°K. The isotherm was identical in shape to the one shown in Fig. 1; therefore, it is not reproduced here. The monolayer volumes were calculated from the B.E.T. equation for the isotherms at both temperatures. They are presented in Table I along with the corresponding surface areas. The swelling process is seen to increase the surface area over its initial value by approximately 5%.

TABLE I

Temperature, °K.	Lower curve		Upper curve	
	V_m, cc. at S.T.P./gm.	S, m.²/gm.	V_m, cc. at S.T.P./gm.	S, m.²/gm.
78	23.81	104.3	25.45	111.5
71	24.96	106.1	25.89	110.0

The isotherms of nitrogen on GF-3 are presented in Figs. 3 and 4. The isotherm depicted in Fig. 3 shows that hysteresis is virtually absent when desorption occurs from moderate relative pressures (less than $p/p_0 = 0.6$). Hysteresis effects are evident in the isotherm shown in Fig. 4 when desorption

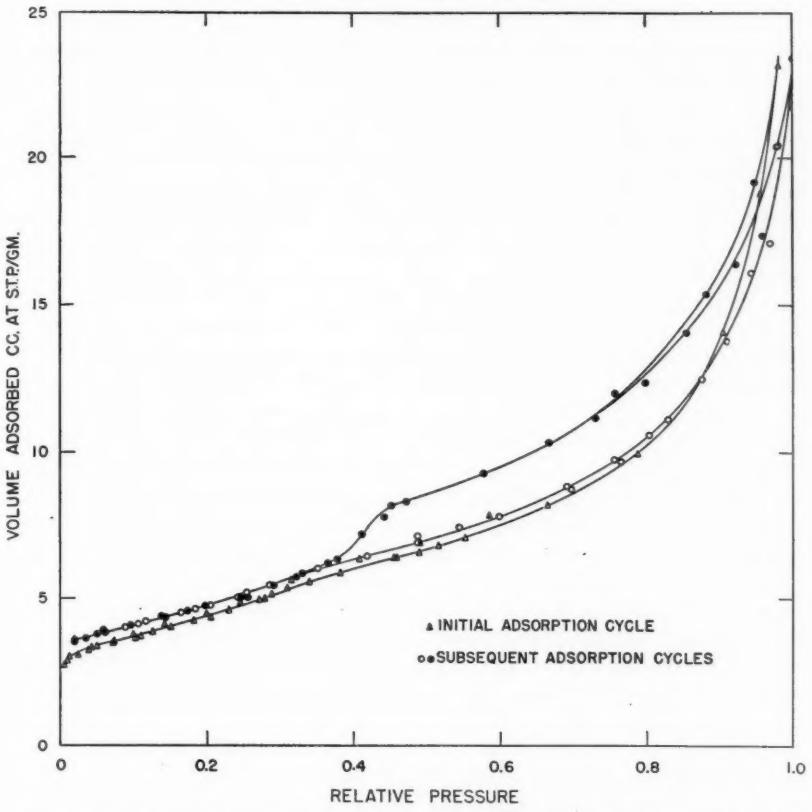

FIG. 4. Isotherm of nitrogen adsorbed by GF-3 at 71°K. Desorption points from the initial adsorption cycle and from subsequent cycles are represented by inked-in circles.

was carried out from relative pressures close to one. The quantity of nitrogen adsorbed by GF-3 is less than that adsorbed by G-3, but the hysteresis effects and the shape of the isotherm have not been changed by removal of most of the ash originally present in G-3. The monolayer volumes and corresponding surface areas for G-3 and GF-3 measured at 71°K. are compared in Table II. The difference between the volumes for upper and lower curves is the same for both graphites.

TABLE II

Graphite	Lower curve		Upper curve	
	V_m, cc. at S.T.P./gm.	S, m.²/gm.	V_m, cc. at S.T.P./gm.	S, m.²/gm.
G-3	4.44	19.0	4.73	20.1
GF-3	3.63	15.9	3.90	17.1

DISCUSSION

It is evident from the foregoing results that Spheron 9 displays hysteresis effects similar to the second type of hysteresis shown by the Acheson graphites. This type of hysteresis has been ascribed to intercrystalline swelling (3). However, the Spheron results differ from those of graphite in one important respect. It was found possible to scan the hysteresis loop of the Spheron isotherm at moderate relative pressures. In contrast the initial adsorption curve for graphite was observed to be more or less reversible at moderate relative pressures (up to $p/p_0 = 0.5$). It was suggested in the earlier paper that the behavior of the graphite system could be explained if the swelling occurred irreversibly at a high relative pressure. Below this relative pressure the initial isotherm would be reversible or nearly so. By the same reasoning one would deduce that the Spheron swells continuously over the whole course of the isotherm. However, even in the case of Spheron the swelling does seem to become irreversible at a high enough relative pressure because the desorption curve from a high relative pressure lies on a reversible isotherm. Arnell and Barss (1) have measured the specific surface of the crystallites of Spheron 9 by X-ray diffraction methods and obtained a value of 1180 $m.^2/gm$. Comparing this value with the surface area of the particle as measured by nitrogen adsorption it can be estimated that each particle is an aggregate of about a thousand crystallites. Biscoe and Warren (2) have shown that the crystallites (or more correctly parallel layer groups) of Spheron 6 (a closely related carbon black) are composed of two-dimensional plane hexagonal nets of carbon atoms separated by essentially the same spacing as in graphite but randomly oriented about a normal to the layers. On the other hand, X-ray diffraction patterns of the Acheson graphites display the sharp lines characteristic of a regular three-dimensional graphite structure. It is logical to attribute the continuous swelling shown by Spheron to the imperfection of the crystallites. It might be expected that the adhesion would be less between the crystallites of Spheron than between those of graphite and consequently swelling occurs continuously from the very onset of adsorption. In the case of graphite a certain reduction of the surface free energy must be attained before any swelling occurs.

The work with GF-3 was undertaken to show that the hysteresis effects were not the result of inhomogeneities in the graphite structure due to the presence of inorganic matter. The isotherm in Fig. 4 demonstrates that neither the shape of the isotherm nor the amount of hysteresis is affected by the amount of ash. However, the quantity of gas adsorbed was found to be somewhat less for the ashless sample.

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REACTION OF OXYGEN ATOMS WITH ACETALDEHYDE[1]

By R. J. Cvetanović

ABSTRACT

Reaction of oxygen atoms, produced by mercury photosensitized decomposition of nitrous oxide, with acetaldehyde has been studied at room temperature. The major products of the reaction are water and biacetyl and the only primary process appears to be

$$CH_3CHO + O \rightarrow CH_3CO + OH \quad [1]$$

followed by

$$CH_3CHO + OH \rightarrow CH_3CO + H_2O \quad [2]$$

and

$$CH_3CO + CH_3CO \rightarrow (CH_3CO)_2. \quad [3]$$

At room temperature oxygen atoms react with acetaldehyde 0.7 ± 0.1 times as fast as with ethylene, so that the activation energy of reaction [1] is likely to be close to 3 kcal./mole.

INTRODUCTION

The present work is the second in a series of investigations of the reactions of oxygen atoms with different organic compounds. In a previous publication (6) the reaction of oxygen atoms with ethylene has been described.

Oxygen atoms are produced by mercury photosensitized decomposition of nitrous oxide. It has been shown (7) that the primary step in this reaction is the formation of an atom of oxygen and a molecule of nitrogen and the rate of nitrogen production serves as a measure of oxygen atoms participating in the process. The important advantage of the use of nitrous oxide, in addition to the presence of an internal actinometer, is the absence of molecular oxygen, which by its rapid reaction with free radicals normally obscures the primary reactions of the atoms.

The reaction of oxygen atoms with acetaldehyde is of considerable interest, particularly in view of its possible participation in the process of oxidation of this compound (2, 3, 12, 13). Avramenko and Lorentso (2, 3) made an attempt to study this reaction directly, by generating oxygen atoms in O_2 and, alternatively, in H_2O. In the former case the mixture from the discharge contained O and O_2, and in the latter case it presumably contained H, O, some OH, the excess H_2O, but almost no O_2. The experiments were performed at 100° C. and the following products were observed: HCHO, CO, CO_2, organic hydroperoxides, CH_3COOH, and some HCOOH. With the H_2O discharge CH_4 and C_2H_4 were also formed. In view of the diversity of the products formed and on the basis of similar experiments with formaldehyde, these authors postulated a variety of primary steps

$$O + CH_3CHO \rightarrow CO_2 + CH_3 + H \quad [4a]$$

$$\rightarrow CHO + HCHO + H \quad [4b]$$

$$\rightarrow CH_3COOH \quad [5]$$

and came to the conclusion that $k_4 > k_5 > k_1$, i.e. that the abstraction of a

[1]*Manuscript received January 26, 1956.*
Contribution from the Divison of Applied Chemistry, National Research Council, Ottawa, Canada. Issued as N.R.C. No. 3953.

single atom of hydrogen was the least probable of the primary processes believed to occur.

The properties ascribed to oxygen atoms by Avramenko and Lorentso are radically different from those usually assumed, notably by Geib (10) who investigated the reaction of oxygen atoms with formaldehyde. Direct experimental evidence, however, is quite scant and in the case of acetaldehyde the paper of Avramenko and Lorentso appears to be the only published work. For this reason the reaction of oxygen atoms, produced by mercury photosensitized decomposition of nitrous oxide, with acetaldehyde has been studied with the object of establishing the primary process and of obtaining some information about the rate of the reaction.

EXPERIMENTAL

The experimental arrangement has been described in detail previously (6). Acetaldehyde was a Matheson Co. product used after thorough degassing and bulb to bulb distillation *in vacuo*.

The products condensable in liquid nitrogen were fractionated on a Le Roy still (11). The "liquid products" were fractionated on a gas–liquid partition chromatographic column (5). Use has also been made of mass-spectroscopic and infrared analysis.

Quantum yields were determined relative to the rate of hydrogen production from 200 mm. of butane at 25° for which Bywater and Steacie (4) find a quantum yield of 0.50. Allowance for a slight drift in the intensity of the incident resonance radiation was made by its frequent determination and interpolation for individual runs.

RESULTS AND DISCUSSION

Relative Quenching Efficiency of Acetaldehyde

In order to establish the suitable range of experimental conditions for the study of the reaction of oxygen atoms with acetaldehyde, it was necessary first to determine the relative quenching efficiency of nitrous oxide and acetaldehyde and the products resulting from the direct mercury sensitized decomposition of the latter compound. The results of experiments with 100 mm. of nitrous oxide and varying amounts of acetaldehyde are given in Table I. Considering for the moment only the series A in Table I, it is seen that with increasing acetaldehyde the quantum yield of nitrogen (ϕ_{N_2}) decreases while the yields of the other observed products relative to R_{N_2}, i.e., to the rate of introduction of oxygen atoms into the process, increase. (With larger amounts of acetaldehyde used in this series of experiments no attempt was made to analyze for such less volatile products as water, biacetyl, or acetone.) The trend in ϕ_{N_2} is due to the competition by the two reactants for the Hg $6(^3P_1)$ atoms and the plot of $1/\phi_{N_2}$ against the acetaldehyde to nitrous oxide ratio can be used in the manner described in an earlier publication (8) to determine the relative over-all quenching efficiency of the two compounds. The plot is given in Fig. 1 and the ratio of the slope to the intercept, i.e., the

TABLE I

MERCURY PHOTOSENSITIZED DECOMPOSITION OF MIXTURES OF 100 MM. OF NITROUS OXIDE AND VARYING AMOUNTS OF ACETALDEHYDE

Run	CH_3CHO, mm.	N_2O, mm.	ϕ_{N_2}	Relative yields of products ($R_{N_2} = 1$)								
				CO	H_2	CH_4	C_2H_6	r.t.*	H_2O	$(CH_3CO)_2$	CH_3COCH_3	$-\Delta CH_3CHO$
Series A. Exposure 90 min., mean $I_a = 3.18 \times 10^{15}$ quanta sec.$^{-1}$, 23±1°C.												
36	127.6	98.9	0.202	1.50	0.321	1.05	0.223					
34	101.0	100.9	0.238	1.21	0.264	0.775	0.203					
37	68.1	100.4	0.311	0.803	0.180	0.422	0.140					
33	42.5	99.9	0.397	0.509	0.121	0.229						
35	20.5	101.3	0.539	0.254	0.040	0.074	0.019					
Series B. Exposure 120 min., mean $I_a = 2.59 \times 10^{15}$ quanta sec.$^{-1}$, 25±1°C.												
56	15.7	100.3	0.572	0.201	0.044	0.050		1.39	1.0	0.4	0.14	3.3
58	4.92	100.4	0.660	0.110	0.019	0.014	0.010	1.42	0.8	0.7	0.10	2.1
60	3.67	100.2	0.667	0.107	0.017	0.010		1.39				1.7
59	3.66	100.6	0.663	0.109	0.012	0.010		1.20				
57	2.52	100.5	0.728	0.141	0.018	0.011	None	1.03	0.6	0.4	0.07	1.4

r.t. = room temperature fraction.

ratio of the over-all quenching efficiency of acetaldehyde to that of nitrous oxide, is 2.28. This value leads to the previously reported (8) relative quenching cross section of acetaldehyde.

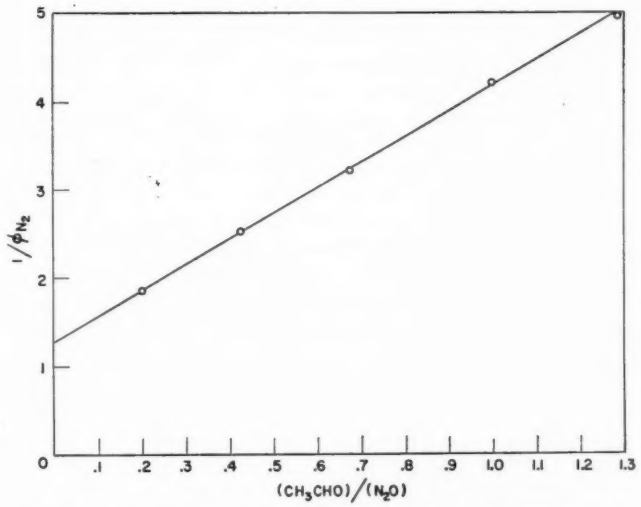

FIG. 1. Plot of the reciprocal quantum yield of nitrogen against $(CH_3CHO)/(N_2O)$ ratio. (100 mm. of N_2O, 23±1°C., mean I_a 3.18×10^{15} quanta/sec., irradiation 90 min.)

Reaction of Oxygen Atoms with Acetaldehyde

The large quenching efficiency of acetaldehyde necessitates small acetaldehyde to nitrous oxide ratios in the study of the reaction of oxygen atoms. At

the same time at too small acetaldehyde pressures there is possibility of secondary reactions of oxygen atoms with the products formed. Fig. 2 shows

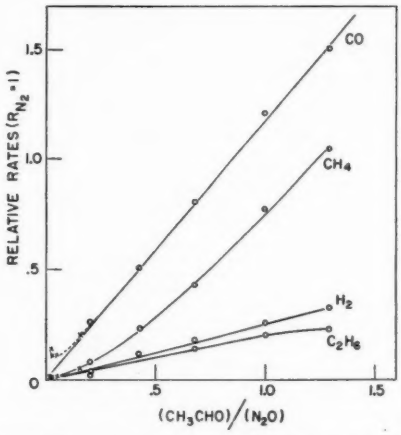

FIG. 2. Relative yields in the mercury photosensitized decomposition of 100 mm. of N_2O and varying amounts of CH_3CHO. Open circles refer to Series A and crosses to Series B, Table I.

a plot of the relative rates of formation of the more volatile products per oxygen atom introduced into the process against the CH_3CHO to N_2O ratio. For Series A the rates of formation of CO, CH_4, H_2, and C_2H_6 extrapolate to zero as the CH_3CHO to N_2O ratio approaches zero, indicating that these

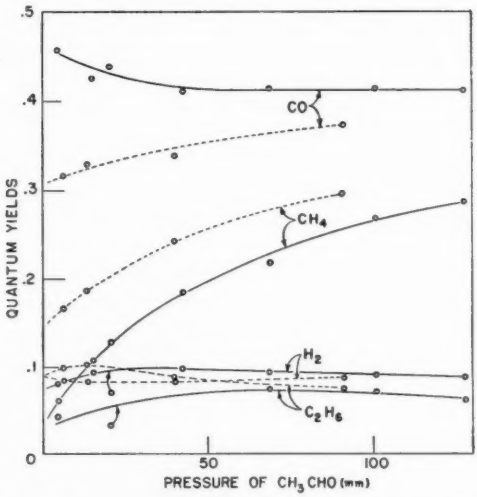

FIG. 3. Quantum yields of gaseous products in the mercury photosensitized decomposition of CH_3CHO alone (broken lines) and of its mixtures with N_2O (continuous lines) as a function of the partial pressure of CH_3CHO.

compounds are due to quenching by acetaldehyde and not to the reaction of oxygen atoms. A few experiments with acetaldehyde alone showed that the same products were formed in the direct mercury sensitized decomposition of this compound. The results are given in Fig. 3 and it is seen that the quantum yields of these products approach at high acetaldehyde pressure those obtained from the mixtures of acetaldehyde and nitrous oxide.* The reasons for the differences at lower acetaldehyde pressures will be discussed after the primary reaction of oxygen atoms with acetaldehyde has been considered.

The results of a number of experiments with lower initial acetaldehyde pressures are given in Table I, Series B. In these experiments it was possible to isolate on the Le Roy still the acetaldehyde fraction (at $-80°$ C.) and subsequently the residual "room temperature" fraction. Both these fractions were analyzed by gas–liquid partition chromatography and by mass-spectrometric methods. The former was found to contain in addition to the unreacted acetaldehyde appreciable amounts of acetone, and the latter large amounts of biacetyl and water. These compounds were not found in the mercury sensitized decomposition of acetaldehyde alone. No other compounds were detected and, in particular, mass spectrometer analysis of the "room temperature" fraction showed absence of acetic acid and alcohols.

The formation of biacetyl and water as the major products under the conditions of the series B of experiments indicates that the following reactions occur:

$$CH_3CHO + O \rightarrow CH_3CO + OH, \quad [1]$$

$$CH_3CHO + OH \rightarrow CH_3CO + H_2O, \quad [2]$$

$$CH_3CO + CH_3CO \rightarrow (CH_3CO)_2. \quad [3]$$

In the absence of any other reactions, the relative rates per oxygen atom would be for water and biacetyl unity and for the consumption of acetaldehyde two. Several other reactions involving CH_3CO radicals must, however, be also considered. Since a certain amount of direct quenching by acetaldehyde occurs even in the experiments where quite small quantities of this compound are used, methyl radicals are also present and their combination with CH_3CO explains the formation of some acetone. Ausloos and Steacie (1) have suggested also abstraction of hydrogen from CH_3CO by CH_3 radicals and disproportionation of two CH_3CO radicals to form ketene and acetaldehyde. In view of this, the relative yield of biacetyl will be lower than unity as a result of the reactions

$$CH_3CO + CH_3 \rightarrow CH_3COCH_3, \quad [6]$$

$$CH_3CO + CH_3 \rightarrow CH_4 + CH_2CO, \quad [7]$$

$$CH_3CO + CH_3CO \rightarrow CH_3CHO + CH_2CO, \quad [8]$$

and possibly to a small extent also

$$CH_3CO \rightarrow CH_3 + CO. \quad [9]$$

At very small acetaldehyde pressures, on the other hand, there is also the possibility of incomplete utilization of O-atoms in reaction [1] and of OH

**The latter quantum yields were calculated relative to the fraction of the incident radiation quenched by acetaldehyde.*

radicals in reaction [2] because of their reactions with the compounds or free radicals formed.* As the acetaldehyde pressure becomes larger the relative yield of biacetyl would be expected to increase and, after reaching a maximum value smaller than unity, to start to decrease again because of the increasing importance of reactions [6] and [7]. The trends in the yields of biacetyl, water, and acetone, and in the consumption of acetaldehyde in the series B of experiments, Table I, are in agreement with these interpretations, although lack of knowledge of the rate constants of the reactions involved and the considerable difficulty of accurately analyzing for these products preclude a detailed quantitative treatment. With the huge amounts of nitrous oxide used no attempt was made to analyze for ketene.

The deviations in Fig. 3 at lower acetaldehyde pressures of the quantum yields of the products resulting from direct quenching by acetaldehyde alone and in the presence of nitrous oxide are understandable in view of the occurrence of reactions [6] to [9]. Methyl radicals are undoubtedly a primary product of the mercury sensitized decomposition of acetaldehyde. Acetyl radicals, on the other hand, appear to be produced in the studied process only by the action of oxygen atoms and then, as a result of reactions [6] and [7], lead to a decrease in CH_3 radical concentration and, therefore, also to a smaller production of methane and ethane (by abstraction and recombination, respectively). The somewhat increased formation of carbon monoxide in the presence of oxygen atoms may be due to some occurrence of reaction [9] and to secondary processes. An evidence for the latter is found in the results given in Table II for a series of experiments with 100 mm. N_2O and 3.6 mm. CH_3CHO

TABLE II

THE EFFECT OF REACTION TIME ON THE RELATIVE YIELDS OF GASEOUS PRODUCT PER OXYGEN ATOM CONSUMED

(Mean I_a 1.76×10^{15} quanta/sec., 100 mm. N_2O and 3.6 mm. CH_3CHO)

Run	Temp., °C.	Irradn., min.	ϕ_{N_2}	Relative yields (R_{N_2} = 1)		
				CO	H_2	CH_4
24	25.3	60	0.64	0.109	0.014	0.011
25	26.2	120	0.65	0.111	0.006	0.017
18	26.9	180	0.64	0.121	0.013	0.007
26	25.7	240	0.66	0.130	0.016	0.009
23	25.1	300	0.65	0.147	0.021	0.009

irradiated for different lengths of time. There is a distinct increase in the relative yield of carbon monoxide with increasing reaction time. The extrapolated initial yields, after allowing for the direct quenching by acetaldehyde, are quite small.

**Various reactions of this type could be suggested, for example those of O-atoms or OH radicals between themselves or with acetyl radicals, leading perhaps in the latter case to the formation of acetic acid. No acetic acid, however, is detected in the product. Although it could be argued that this compound might undergo further attacks once it is formed, postulates of this kind would be very speculative in the absence of any supporting evidence. At present it would seem better not to attempt to specify these processes in any detail. Their net effect, as well as of possible analogous reactions involving the products, must be a decrease in the yields of biacetyl and water at very small acetaldehyde pressures.*

The present experiments indicate that the only mode of reaction of oxygen atoms with acetaldehyde is the abstraction of the aldehydic hydrogen atom to give an OH and a CH_3CO radical. This result is in disagreement with the postulates of Avramenko and Lorentso (2, 3), who consider the abstraction of the hydrogen atom to be the least probable of the assumed several distinct modes of primary reaction. It ought to be pointed out, however, that the experiments of these authors were conducted at a higher temperature where CH_3CO radicals are known to decompose readily. A further complicating feature might have been the presence of relatively large concentrations of hydrogen atoms and possibly also of some molecular oxygen even in the H_2O discharge.

Estimate of the Activation Energy of the Reaction

In order to obtain information on the rate of the reaction of oxygen atoms with acetaldehyde, several experiments were conducted at 25° C. with mixtures of 300 mm. of N_2O and varying ratios of smaller amounts of CH_3CHO and C_2H_4. To minimize any depletions of the reactants in the course of the reaction a circulating system of total volume 500 ml. was employed. The results are given in Table III. Direct quenching by C_2H_4 resulted, at the high total

TABLE III

EXPERIMENTS WITH MIXTURES OF 300 MM. OF N_2O AND VARYING AMOUNTS OF CH_3CHO AND C_2H_4 (25±1°C., CIRCULATING SYSTEM)

Run	CH_3CHO, mm.	C_2H_4, mm.	$\frac{CH_3CHO}{C_2H_4}$	Irradn., min.	R_{N_2}, molec.cc.$^{-3}$ sec.$^{-1}$ $\times 10^{-15}$	Relative rates (R_{N_2} = 1)			
						CO	CH_4	H_2	$-\Delta C_2H_4$
73	—	51.3	—	65	1.23	0.471	0.146	0.078	
72	4.83	51.6	0.094	60	1.21	0.448	0.143	0.095	
71	5.15	19.9	0.259	60	1.42	0.404	0.125	0.072	
70	4.90	9.94	0.493	60	1.49	0.378	0.117	0.064	0.917
69	4.73	4.94	0.961	60	1.51	0.332	0.106	0.068	
76	2.44	1.06	2.30	60	1.69	0.251	0.048	0.059	0.484
78	4.90	1.06	4.64	60	1.63	0.244	0.040	0.043	0.280
79	7.92	1.06	7.49	60	1.71	0.185	0.036	0.040	
81	8.03	1.06	7.61	120	1.79	0.189	0.035	0.041	0.190
75	4.74	0.524	9.05	60	1.64	0.179	0.030	0.043	
74	4.82	—	∞	60	1.63	0.126	0.010	0.002	—

NOTE: *the R_{N_2} values are not strictly comparable between themselves since the reaction cell was occasionally flamed and the transparency of the front window fluctuated to some extent. Mean I_a remained about 2.3×10^{15} quanta/sec.*

pressures used, in essentially complete collisional deactivation. The processes to be considered in addition to reactions [1] and [2] are

$$C_2H_4 + O \rightarrow \text{Products} \qquad [10]$$

and

$$C_2H_4 + OH \rightarrow \text{Products}. \qquad [11]$$

The products of reaction [10] are known (6, 9), while no information on reaction [11] appears to be available. It will be assumed, subject to subsequent justification, that reaction [11] cannot compete successfully with reaction [2]

for OH radicals under the conditions of the experiments performed. It is then possible to evaluate k_1/k_{10} by comparing the relative rates of formation of different products or of the consumption of the reactants as CH_3CHO to C_2H_4 ratio is varied, since it was found that this ratio remained virtually unaltered in the course of reaction with the amounts and conversion levels used. Thus, in the reaction of oxygen atoms with about 1 mm. ethylene in the presence of 300 mm. N_2O the relative rate of over-all consumption of ethylene per oxygen atom is about 1.2. If in the mixtures of C_2H_4 and CH_3CHO the latter compound does not interfere with the reaction of O-atoms with ethylene except by using some of the available O-atoms, the following relationship would be expected to hold

$$\frac{R_{N_2}}{R_{C_2H_4}} = 1.2\left(1 + \frac{k_1}{k_{10}}\frac{(CH_3CHO)}{(C_2H_4)}\right).$$

The plot of $R_{N_2}/R_{C_2H_4}$ vs. $(CH_3CHO)/(C_2H_4)$ is given in Fig. 4 and the value of k_1/k_{10} obtained from the slope to intercept ratio is 0.68. In a similar manner,

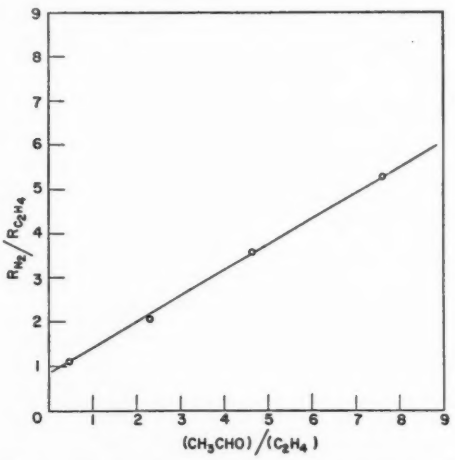

FIG. 4. Plot of the reciprocal rate of C_2H_4 consumption per oxygen atom vs. $(CH_3CHO)/(C_2H_4)$ ratio.

if any one of the relative rates per oxygen atom ($\zeta = R/R_{N_2}$) has a value α with C_2H_4 alone and β with CH_3CHO alone, then

$$\epsilon = \frac{\zeta - \alpha}{\beta - \zeta} = \frac{k_1}{k_{10}}\frac{(CH_3CHO)}{(C_2H_4)}.$$

In Fig. 5 are given the plots of ϵ against $(CH_3CHO)/(C_2H_4)$ for CO and CH_4 with the respective α and β values as found experimentally in runs 73 and 74 (Table III). There is a considerable scatter of points, which is readily explainable by limitations in analytical accuracy. A corresponding plot for the relatively small H_2 production is for the same reason much too uncertain, although the

trend is qualitatively the same. The results for CO and CH_4 are mutually in reasonably good agreement and the slope of what appears to be the best line through the points gives 0.64 as the value of k_1/k_{10}.

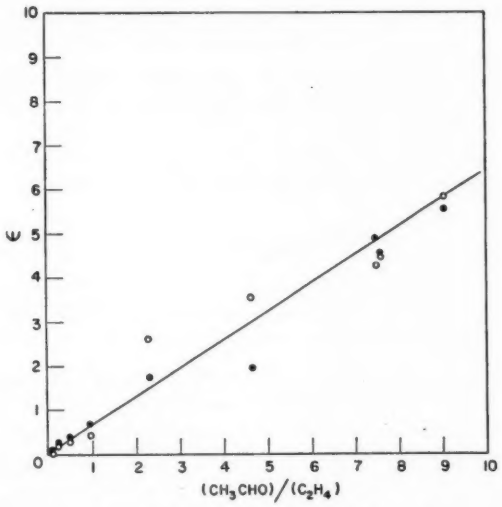

FIG. 5. Plots of ϵ_{CH_4} (open circles) and ϵ_{CO} (filled circles) vs. $(CH_3CHO)/(C_2H_4)$ ratio.

The value of k_1/k_{10} can also be estimated by comparing the rates of consumption of the two reactants. If the over-all consumption of C_2H_4 per oxygen atom is about 1.2 and that of CH_3CHO is presumably 2, the following relationship would be expected to hold

$$\frac{k_1}{k_{10}} = \frac{1.2}{2} \frac{(C_2H_4)}{(CH_3CHO)} \frac{R_{CH_3CHO}}{R_{C_2H_4}}.$$

It is difficult to determine accurately the rate of CH_3CHO consumption, in particular since some aldehydes are a product of the reaction of O-atoms with C_2H_4 (6). However, by applying reasonable corrections the values of R_{CH_3CHO} in addition to the corresponding $R_{C_2H_4}$ were obtained for two runs. In both cases k_1/k_{10} was thus found to be somewhat larger than 0.6 with probable uncertainty not greater than about 20%.

The values of k_1/k_{10} obtained in different ways are therefore mutually consistent and it appears reasonably certain that at room temperature $k_1/k_{10} = 0.7 \pm 0.1$. In view of this it is likely that E_1 is close to 3 kcal./mole, the value recently estimated (6) for reaction [10]. The work now in progress with a number of olefinic hydrocarbons with the use of improved analytical techniques (5) may provide means for additional verification of these values and for eventual determination of the activation energy differences for a number of reactions of oxygen atoms with common organic compounds.

The consistency of the k_1/k_{10} values obtained in different ways provides justification for the earlier made assumption that OH radicals react preferentially with acetaldehyde. The alternative assumption that in the performed experiments oxygen atoms reacted exclusively with CH_3CHO and that the observed trends were due to a competition for OH radicals rather than for O-atoms is highly unlikely. This assumption would require that OH radicals form with ethylene the same type of products and moreover in the same ratio as are formed in the interaction of oxygen atoms with ethylene. The results in Table III show that the yields of CO, CH_4, and H_2 approach those obtained with C_2H_4 alone as the $(CH_3CHO)/(C_2H_4)$ ratio approaches zero and in the reaction of O-atoms with C_2H_4 no OH radicals are formed.

ACKNOWLEDGMENT

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THE COMPOSITION OF THE STRONG PHOSPHORIC ACIDS[1]

By Anna-Liisa Huhti and Phoebus A. Gartaganis

ABSTRACT

The composition of the strong phosphoric acids was studied in the range 68.8 to 86.3% phosphorus pentoxide by weight. Improved filter-paper chromatography made possible the quantitative determination of the nine lower members of the series, and occasionally up to the twelfth member. It was found that when the strong phosphoric acids are prepared by heating at 350°C., a dynamic equilibrium between the component acids is set up which persists when the mixtures are cooled to room temperature. Only linear condensed polyphosphoric acids were present in the range studied. The composition corresponding to 100% orthophosphoric acid contains about 6 mole per cent each of pyrophosphoric acid and "free water". As the mole ratio of water to phosphorus pentoxide decreases, the number of component acids increases. Orthophosphoric acid is present to an appreciable extent in the stronger phosphoric acids. "Hexametaphosphoric acid" is not a separate chemical entity, but a mixture of higher linear polyphosphoric acids.

INTRODUCTION

The composition of the strong phosphoric acids,* i.e. acids containing more than 72.4% by weight of phosphorus pentoxide, the P_2O_5 content of pure orthophosphoric acid, is a subject of considerable interest which has been repeatedly investigated by wet analytical methods. Difficulties in these methods, however, have set a decided limitation on the qualitative and quantitative conclusions possible. A study of this subject by filter-paper chromatography was undertaken, therefore, in order to obtain further and more specific information about compositions having a mole ratio of water to phosphorus pentoxide between 3.6 and 1.2.

It has been shown by means of paper chromatography that by mixing orthophosphoric acid with phosphorus pentoxide at different ratios, and heating the mixture at 350°C., we obtain a mixture containing only linear condensed polyphosphoric acids. No cyclic ones were found. Branched acids, if present, would not be detected, since any ion-molecules with branching are expected to hydrolyze immediately upon dissolution (40). A certain characteristic equilibrium mixture exists for every given ratio of water to phosphorus pentoxide.

The phosphoric acids are very viscous, so that equilibria are attained very slowly; the end result of cooling is an oil in the range 72 to 82% P_2O_5, a gum in the range 82 to 86% P_2O_5, and a brittle glass at higher P_2O_5 concentrations. These acids are merely members of a continuous series of amorphous condensed phosphoric acid mixtures which extends from orthophosphoric acid to pure phosphorus pentoxide (38). These mixtures are hygroscopic and hydrolyze upon standing unless stored in tightly closed pyrex containers.

The existence of strong phosphoric acids has been known for many years. Durgin, Lum, and Malowan (14) give a list of several such acids reported

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Contribution from the Department of Chemistry, Ontario Research Foundation, Toronto 5, Ontario.

**A commercial term, a high degree of ionization not necessarily implied.*

previously in the literature. Some of these have since then been positively identified, e.g. the tetrapolyphosphoric acid, $H_6P_4O_{13}$, while for others there is enough evidence to date to make their existence highly improbable, e.g. the metaphosphoric acid monomer, HPO_3. Finally, some of the acids listed by the above-mentioned authors, which at the time represented merely theoretical combinations of phosphorus pentoxide and water, have during the present study been positively identified as far as this is possible by paper chromatography, and their relative concentrations in several mixtures accurately established, e.g. "hexerohexaphosphoric" acid, $H_8P_6O_{19}$, better known today as hexapolyphosphoric acid. The same authors checked the analytical methods of Gerber and Miles (19) against those of Britske and Dragunov (6) and found an increasing divergence when acids of high phosphorus pentoxide content were being analyzed. This they considered as evidence that polyphosphoric acids may be present in the strong phosphoric acids.

Bell (3) went a step further by recognizing that tripolyphosphoric acid is present and interferes in some procedures for pyrophosphate determination. By using an analytical method previously developed by the same author (5), he was able to show the presence of ortho-, pyro-, and tripolyphosphoric acids in several of the strong phosphoric acid mixtures, and of "the polymer of metaphosphoric acid commonly known as hexametaphosphoric acid". An "unidentified" acid, indicated by difference, was also present between 78 and 88% phosphorus pentoxide.

Although the exact composition of the strong phosphoric acid mixtures had not been established, several of their physical and chemical properties as a function of their phosphorus pentoxide content were reported in the literature. These include, among others, measurements of densities (14, 23), viscosities (14), vapor pressures (7), boiling points and composition of the vapor over the boiling mixture (38), and heats of vaporization (38). By boiling orthophosphoric acid an azeotropic mixture was obtained (b.p. 869°C., 753 mm. Hg) containing 92.1% phosphorus pentoxide (34). Vapor-density measurements indicated that the vaporized acids dissociate into water and phosphorus pentoxide at temperatures near 1000°C. (38).

EXPERIMENTAL AND RESULTS

Analytical Methods

Various methods exist for the analysis of phosphate mixtures. Considerable effort has been spent during the last 50 years on developing traditional wet-chemical methods (2, 3, 6, 15, 19, 25, 33) for determining the various species of phosphates in the presence of one another. These methods were not adequate since they could not separate the acids higher than tripolyphosphoric acid. These higher acids are present in many strong phosphoric acid mixtures and interfere with the analysis. None of the methods has proved very satisfactory. This has recently been clearly demonstrated for mixtures of pyro- and tripolyphosphate by Dewald (13). The most commonly used wet-chemical methods are those of Jones (24) and Bell (5). Both these procedures are satisfactory for routine determinations on a given industrial product, although the absolute values may be considerably in error. According to the

Bell procedure, no distinction is possible between polyphosphates with more than four phosphorus atoms in their chain. The zinc precipitation method of Raistrick, Harris, and Lowe (28) does not tolerate large amounts of orthophosphate, while the various X-ray methods, such as the one developed by Raistrick (27), are of course limited to crystalline mixtures. The temperature rise method of McGilvery (26) has so far only found application to sodium tripolyphosphate mixtures containing Phases I and II. The infrared technique of Corbridge and Lowe (10) is sensitive to differences of crystalline form but quantitative methods for amorphous phosphates have not been reported. The sensitivity of the end-group titration methods of Samuelson and Van Wazer (32, 40) decreases with increasing chain length.

As compared with these methods, the paper chromatographic procedure combined with differential spectroscopy (18) permits the direct determination of more species of phosphate anions with as good or better accuracy.

Chromatographic Analysis

The analyses were made using a procedure developed in this laboratory and described in previous papers (11, 42). This method involves the separation of the phosphate components by filter-paper chromatography and the subsequent colorimetric determination of the phosphorus content of each component. The precision of the method is an absolute figure varying from ± 0.5 to $\pm 1.0\%$ of the total phosphorus present, depending on the number and species of phosphates present.

The following modifications of the above-mentioned method have been introduced. In addition to the rectangular chromatographic tanks already in use, cylindrical containers (height 43 cm., diameter 24 cm.) were employed to perform bidimensional base–acid analyses as described by Ebel and his coworkers (16). This method makes possible the clear separation and differentiation of condensed cyclic and linear polyphosphates. The phosphate solution was spotted at the base of a cylindrically shaped 58×22 cm. Schleicher and Schuell No. 589 Green Ribbon filter paper, placed inside the cylindrical tank. This was filled 1 cm. deep with the basic solvent (17) consisting of

40 cc. isopropanol,
20 cc. isobutanol,
39 cc. water,
1 cc. ammonia (25%).

After 24 hr. the paper was dried and placed in a tank containing the acid solvent (31) consisting of

70 cc. isopropanol,
20 cc. trichloracetic acid (25%),
10 cc. water,
0.3 cc. ammonia (25%).

This solvent is very similar to those described by Volmar, Ebel, and Yacoub (16), and Grunze and Thilo (22). The direction of movement of the solvent in the two cases were perpendicular to each other.

The method of Consden, Gordon, and Martin (9), which uses filter-paper chromatograms with downward solvent flow, has been abandoned in favor of ascending chromatographic techniques. The resulting slowing down of the movement of the solvent produced a better separation of phosphates with chains from 5 to 11 phosphorus atoms. The paper was cut in strips approximately 30×13 cm., with the lower end pointed and ending in a narrow projection, 1 cm. wide, dipping into a beaker filled with fresh solvent.

The running time varied from 16 to 24 hr., the temperature being kept constant at 17°C. No correction was made for any hydrolysis occurring during the running of the chromatogram. Hydrolysis studies since show that the principal effect of hydrolysis would be to reduce the values for hypoly- and raise that for pyro- and to a lesser extent ortho-. Intermediate chain lengths would probably gain as much as they would lose. The hydrolysis error was estimated not to exceed one per cent of the total phosphorus in the values given in Table III except in the cases where hypoly- is a major constituent, in which case the hypoly- may be underestimated by as much as 20% of its true value, the other components being uniformly overestimated accordingly. It has not been possible to compare against standard solutions in the case of acids with more than four phosphorus atoms, since they have so far not been isolated.

Materials

Orthophosphoric acid, 85%, 0.0001% As, Merck (87.1% H_3PO_4 by analysis).

Phosphorus pentoxide, min. 98%, 0.005% As, Merck (98.0% P_2O_5 by analysis).

Sodium phosphate monobasic monohydrate, Merck, $NaH_2PO_4.H_2O$.

Sodium phosphate dibasic anhydrous, Merck, Na_2HPO_4.

Sodium pyrophosphate decahydrate, Merck, $Na_4P_2O_7.10H_2O$.

Sodium tripolyphosphate anhydrous, techn. ERCO. Purified by successive recrystallizations from an ethanol–water mixture.

Sodium tetrapolyphosphate. Sodium tetrametaphosphate was hydrolyzed in a 5 *N* sodium hydroxide solution, and precipitated as an oil with ethanol.

Sodium trimetaphosphate. $NaH_2PO_4.H_2O$ was heated four hours at 1100°C. and then 24 hr. at 550°C. It was recrystallized from aqueous solution with ethanol.

Sodium tetrametaphosphate (Cyclophos), Victor Chemical Works. Purified by successive recrystallizations from an ethanol–water mixture.

Preparation of the Acids

A series of mixtures having a mole ratio of H_2O to P_2O_5 between 3.6 and 1.2, i.e. a phosphorus pentoxide content between 68.8 and 86.3% by weight, were prepared by placing 15 to 25 gm. phosphoric acid and phosphorus pentoxide in a 50-ml. Erlenmeyer flask, flame sealing, and heating it in a furnace at approximately 350°C. for about 10 to 20 min. Vigorous shaking in the furnace helped to obtain a uniform mixing of the materials. The heating was interrupted before or immediately after the acids started to attack the Pyrex container. After the mixture had cooled to room temperature, the flask was broken open; a sample was withdrawn and neutralized with 1 *N* sodium

hydroxide to the phenolphthalein end point. All the strong phosphoric acids hydrolyze when dissolved in water and revert finally to orthophosphoric acid. The rate of hydrolysis (12, 21, 39) is very dependent on temperature and the pH of the solution; at room temperature and at a pH 8 to 10 the rate is extremely slow. In order to prevent hydrolysis, care was taken to dilute the acid mixture as quickly as possible, while keeping the pH near the phenolphthalein end point and cooling the sample in crushed ice. A small drop of this solution was analyzed by means of paper chromatography.

For several samples, the phosphorus pentoxide content, calculated from the weight of the starting materials, was found to be in agreement with the total P_2O_5 determined by direct pH titration (1) after complete hydrolysis.

Preliminary experiments were used to assess the importance of the experimental conditions.

(*a*) It was soon established that the relative proportion of the component phosphoric acids is a function of the over-all concentration of phosphorus pentoxide only and does not depend on the method of preparation. Mixtures were prepared by evaporating orthophosphoric acid in pyrex containers, in a graphite crucible, and in a platinum crucible respectively. In each case the composition of the mixture obtained corresponded to that found when the acids were prepared in sealed Erlenmeyer flasks. Durgin *et al.* (14) and Bell (3) arrived earlier at the same conclusion.

(*b*) As shown in Table I, the time of heating had no significant effect on the analysis of the solutions obtained, provided a clear melt was obtained before the glass was attacked.

TABLE I

EFFECT OF TIME OF HEATING ON COMPOSITION OF STRONG PHOSPHORIC ACID MIXTURES (P_2O_5 content: 77.6%; temperature: 300°C.)

Time (min.)	Distribution of total phosphorus (wt. %)				
	Ortho-	Pyro-	Tri-	Tetra-	Penta-
3	30.9	48.5	14.8	4.3	1.5
5	31.0	48.3	15.7	3.9	1.1
10	32.9	48.1	14.4	3.8	0.8
30	32.6	47.6	14.3	4.5	1.0

TABLE II

EFFECT OF TEMPERATURE OF PREPARATION ON COMPOSITION OF STRONG PHOSPHORIC ACID MIXTURES (P_2O_5 content: 77.6%; heating time: 5 min.)

Temp. (°C.)	Distribution of total phosphorus (wt. %)				
	Ortho-	Pyro-	Tri-	Tetra-	Penta-
250	30.6	49.3	14.5	4.8	0.8
300	32.0	47.9	14.3	4.6	1.2
344	30.9	48.2	14.8	4.8	1.3
405	30.8	48.8	14.7	4.8	0.9

(*c*) The effect of the temperature of preparation on the composition of the mixture is shown in Table II. It will be noted that the temperature range covered was not very large, but was sufficient to show that the temperature of preparation was not a critical factor in these experiments.

The principal experiments were concerned with mixtures having a phosphorus pentoxide content ranging from 68.8 to 86.3%. The results are presented in Table III and plotted in Figs. 2 and 3. In the latter the vertical distance between the curves represents the concentration of the phosphoric acid indicated by number, expressed in per cent P_2O_5 by weight.

TABLE III

COMPOSITION OF STRONG PHOSPHORIC ACIDS

Composition (wt. % P_2O_5)	Per cent of total phosphorus as:									
	Ortho-	Pyro-	Tri-	Tetra-	Penta-	Hexa-	Hepta-	Octa-	Nona-	"Hypoly-"
68.80	100.00	Trace								
69.81	97.85	2.15								
70.62	95.22	4.78								
72.04	89.91	10.09								
72.44	87.28	12.72								
73.43	76.69	23.31								
74.26	67.78	29.54	2.67							
75.14	55.81	38.88	5.31							
75.97	48.93	41.76	8.23	1.08						
77.12	39.86	46.70	11.16	2.28						
78.02	26.91	49.30	16.85	5.33	1.60					
78.52	24.43	48.29	18.27	6.75	2.26					
79.45	16.73	43.29	22.09	10.69	4.48	1.92	0.80			
80.51	13.46	35.00	24.98	13.99	6.58	3.14	2.84			
81.60	8.06	27.01	22.28	16.99	11.00	5.78	3.72	2.31	1.55	1.28
82.57	5.10	19.91	16.43	16.01	12.64	8.89	6.41	4.11	3.51	6.99
83.48	4.95	16.94	15.82	15.91	12.46	9.71	6.77	5.04	2.99	9.42
84.20	3.63	10.60	11.63	13.05	12.17	9.75	8.19	5.92	4.91	20.16
84.95	2.32	6.97	7.74	11.00	10.45	9.62	8.62	7.85	6.03	29.41
86.26	1.54	2.97	3.31	5.16	5.32	5.54	3.51	3.30	3.30	66.03

N.B. The figures are given to two decimal places for further computation purposes, but the precision may not be better than one per cent total phosphorus in some cases.

DISCUSSION

Both our work and that of earlier authors support the view that, when the strong acids are prepared by heating, a dynamic equilibrium between the component acids is set up which is metastably frozen in when the mixtures are cooled to room temperature. Methods used to date to study these mixtures have been largely based on analytical or crystallization techniques.

Analysis

Our analyses based on paper chromatography agree roughly with those of Bell (3) based on wet-chemical methods as far as the low molecular weight components are concerned; it appears, however, that what he considered to be tripolyphosphate was actually a mixture of this and various other acids with longer chains. Indeed, as can be seen from Fig. 1, the maximum of the tripolyphosphoric acid curve is at about 25% whereas a maximum of about 60% was reported by Bell for this member of the series. It is conceivable that tetrapolyphosphoric (4) and probably some acids with longer chains would respond to the same analytical test used in the determination of tripolyphosphoric acid by the Bell (3) method.

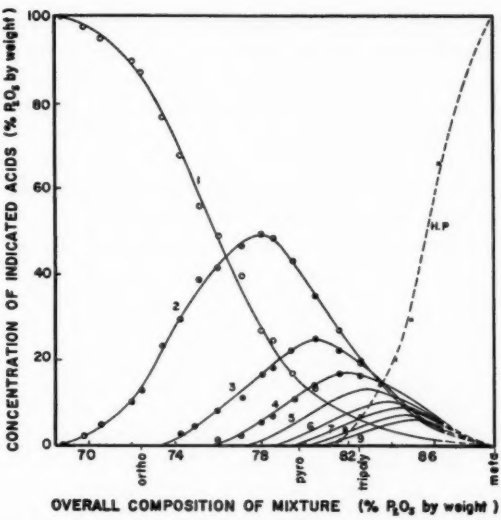

FIG. 1. The composition of the strong phosphoric acids (weight basis); 1 = ortho-, 2 = pyro-, 3 = tri-, 4 = tetra-, 5 = penta-, 6 = hexa-, 7 = hepta-, 8 = octa-, 9 = nona-, and H.P. = "hypoly-".

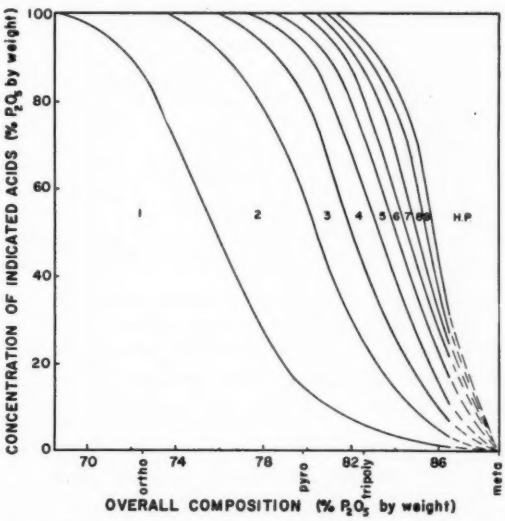

FIG. 2. The composition of the strong phosphoric acids (cumulative) (weight basis); 1 = ortho-, 2 = pyro-, 3 = tri-, 4 = tetra-, 5 = penta-, 6 = hexa-, 7 = hepta-, 8 = octa-, 9 = nona-, and H.P. = "hypoly-".

The "unidentified" acid, believed by him to be a lower polymer of metaphosphoric acid, was found to correspond to the positions of the penta- and hexaphosphoric acids.

A clear separation from the starting line with complete absence of 'ghosting' was noted up to about 83% phosphorus pentoxide content. This behavior is not found when highly polymerized phosphates are chromatographed; from this it was inferred that the acids analyzed as higher polyphosphoric acids (H.P.) were linear acids with not very long chains.

The acid reported by Bell (3) as "hexametaphosphoric acid", a name originally used by Remziye (30) to describe the acid which coagulated albumin, is not a single species. The line indicated in Fig. 1 by H.P., corresponding to Bell's "hexametaphosphoric acid", has no physical meaning and is given for reference reasons only; it includes all acids with a chain containing more than nine phosphorus atoms. Although at times a good separation was possible up to the dodecapolyphosphoric acid, all the results for reasons of uniformity are reported up to the nonapolyphosphoric acid only.

Thilo and Sauer (35), by applying Ebel's bidimensional technique to the investigation of mixtures of phosphoric acids obtained by dehydration of orthophosphoric acid, have confirmed our observation that only linear polyphosphoric acids were present. Traces of cyclic acids were observed in mixtures containing over 84% phosphorus pentoxide. Any branched members are believed (40) to be very unstable in aqueous solution and will degrade to form linear phosphates before any known analytical method can be applied. It is interesting to note that orthophosphate ion is present to an appreciable extent in the strong phosphoric acids. On the contrary, earlier studies (36, 41) showed that glasses in the sodium oxide – phosphorus pentoxide system contain no detectable amounts of orthophosphate. According to Van Wazer (8, 37) "in the derivation of the theoretical distribution function for these glasses, no orthophosphate appeared, because a single PO_4 group with three negative charges would represent a high charge concentration which would violate the law of detailed distribution of charge". A similar calculation in the case of the acids was inconclusive. However, Van Wazer was able to explain the presence of orthophosphate ions in the acids as follows: "The presence of orthophosphate in the equilibrium mixture of strong phosphoric acids shows that some of the hydrogen atoms are covalently bound to PO_4 groups, so that the monohydrogen orthophosphate ion can be considered as being uniomized in these concentrated acids. Naturally this conclusion is in agreement with the very small ionization constant of the $HPO_4^=$ ion in dilute aqueous solution".

Crystallization

The strong phosphoric acid mixtures crystallize upon standing. Rakuzin and Arseniev (29) obtained from a mixture containing 84% phosphorus pentoxide, corresponding to the P_2O_5 content of the pure tetrapolyphosphoric acid, a crystalline product after five days of standing. A description by these authors of the solid obtained indicates that the reported crystals were actually pyrophosphoric acid; this lower-strength acid might have been formed by the absorption of moisture from the air (14).

More careful studies by Gerber and Miles (19), Bell (3), and this laboratory showed that mixtures with a phosphorus pentoxide composition corresponding

to the P_2O_5 content of pyrophosphoric acid crystallized on standing. The partially crystallized mixture contained more pyrophosphoric acid than the original mixture but, on remelting, the composition returned to that of the original mixture before crystallization.

All methods of investigation, such as crystallization, which involve a change of phase need careful interpretation. It should not be overlooked that the composition of the primary phase separating from a homogeneous phase containing more than one component may bear no relation to the constitution of that phase.

Calculations

By making certain assumptions, it is possible to transform the data of Table III from a weight per cent to a mole per cent basis, and, by using a suitable scale of abscissae, to bring out certain relationships.

The assumptions are:

(*a*) The component acids (and water) can be represented by the general formula $H_{n+2}P_nO_{3n+1}$, where $n = 0, 1, 2, \ldots$. This enables a free water content to be calculated when the component acids can be determined completely. This water is free only in the stoichiometric sense, i.e. it is not combined with P_2O_5 to form a component acid. Probably it is strongly solvated by H_3PO_4, here considered the solvent, since it is the predominant component, and this may account for the simultaneous presence of water and condensed acids in an equilibrium mixture.

(*b*) By extrapolation of calculated "free water" contents, it is assumed that there is no actual "free water" in compositions studied containing more P_2O_5 than the 80.51% mixture. This enables a number average molecular weight to be calculated for the "hypoly" fraction. It neglects the traces of ring compounds present in compositions over 84% phosphorus pentoxide.

The recalculated results are shown in Table IV and are plotted, for the lower acids, in Fig. 3. This figure shows clearly that, as the phosphorus content of the mixture increases, pyrophosphoric acid and "free water" appear before

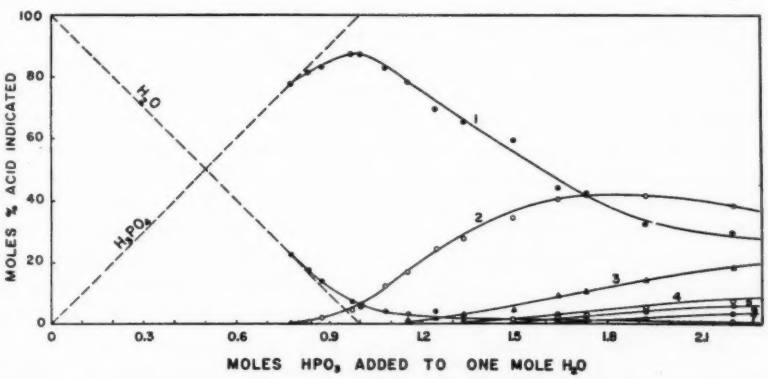

FIG. 3. Computed composition of the strong phosphoric acids (mole basis); 1 = ortho-, 2 = pyro-, 3 = tri-, 4 = tetra-, 5 = penta-, 6 = hexa-, 7 = hepta-.

the over-all composition reaches that of H_3PO_4. At this composition there is only about 88 mole per cent H_3PO_4, with about 6 mole per cent each of "free water" and pyrophosphoric acid. Thus, many of the published properties of "100% H_3PO_4" are subject to a new interpretation.

TABLE IV

COMPOSITION OF STRONG PHOSPHORIC ACIDS
(AND NUMBER AVERAGE CHAIN LENGTH OF "HYPOLY" FRACTION)

Over-all composition (moles HPO_3/mole H_2O)	Composition in terms of component acids and water (mole per cent)											Number average chain length
	$n = 1$	2	3	4	5	6	7	8	9	"Hypoly"	Free water	
0.7773	77.74										22.26	
0.8308	81.29	0.90									17.81	
0.8780	83.60	2.10									14.30	
0.9718	87.35	4.90									7.75	
1.0012	87.61	6.38									6.01	
1.0805	82.88	12.60									4.52	
1.1554	78.30	17.07	1.03								3.61	
1.2447	69.48	24.20	2.20								4.12	
1.3403	65.61	27.99	3.67	0.36							2.37	
1.4952	59.60	34.91	5.56	0.85							−0.92	
1.6397	44.09	40.38	9.21	2.18	0.52						3.64	
1.7310	42.25	41.77	10.54	2.92	0.78						1.74	
1.9269	32.22	41.69	14.18	5.15	1.72	0.62	0.22				4.20	
2.2041	29.61	38.49	18.31	7.70	2.89	1.14	0.89				0.97	
2.5751	21.52	35.97	19.78	11.32	5.86	2.57	1.41	0.77	0.45	0.35		0.9
3.0156	16.48	32.18	17.70	12.93	8.18	4.78	2.96	1.66	1.26	1.87		2.5
3.5765	16.85	28.83	17.96	13.55	8.48	5.51	3.28	2.14	1.12	2.26		—
4.1797	15.17	22.15	16.20	13.65	10.18	6.79	4.89	3.09	2.28	5.60		15.0
5.0519	11.72	17.61	13.03	13.89	10.56	8.11	6.21	4.95	3.38	10.53		14.1
7.8421	12.08	11.65	8.67	10.12	8.35	7.25	3.92	3.25	2.86	31.84		16.3

Figure 3 is also interesting in that it shows that "free water" is present in acid mixtures much higher in phosphorus content than the composition H_3PO_4. When the molecular weight of water, in comparison with the component acids, is considered, a more or less smooth curve for "free water" is obtained, indicating the consistency of the data, until the more complex mixtures are encountered. Here, the analytical difficulties, number of components, and high molecular weights influence the "free water" calculation adversely, although analytical errors in the low molecular weight components may have the greatest effect. Analytical errors which compensated in such a way as not to change the observed number average molecular weight of the component acids would not be detected by this test.

The number average chain lengths calculated for the "hypoly" fraction are shown in Table IV. The inconsistency of the values for the first three mixtures is probably due to the small amounts of the "hypoly" present; however, the number average chain length appears to reach a constant value of about 16 in the rest of the cases, although the amount of "hypoly" increases from 20 to 66% phosphorus pentoxide by weight. Such a maximum might be due to a changing distribution of the molecular weight or the appearance of ring polymers. The latter were not detected chromatographically to any appreciable extent in the compositions analyzed. It is remarkable that the maximum mole per cent is still in the pyrophosphate range, even when about 32 mole per cent of "hypoly" is present. Finally, the general shapes of the curves in Fig. 3 are such that they might be roughly expressed in terms of mass law constants. The average K value, based on concentrations, for the

second to fifth mixtures in Table IV is 5×10^{-3} (2.43, 4.30, 4.98, 4.99, 8.29 respectively). At most, these indicate some tendency towards a constant value, which might be revealed by more accurate data.

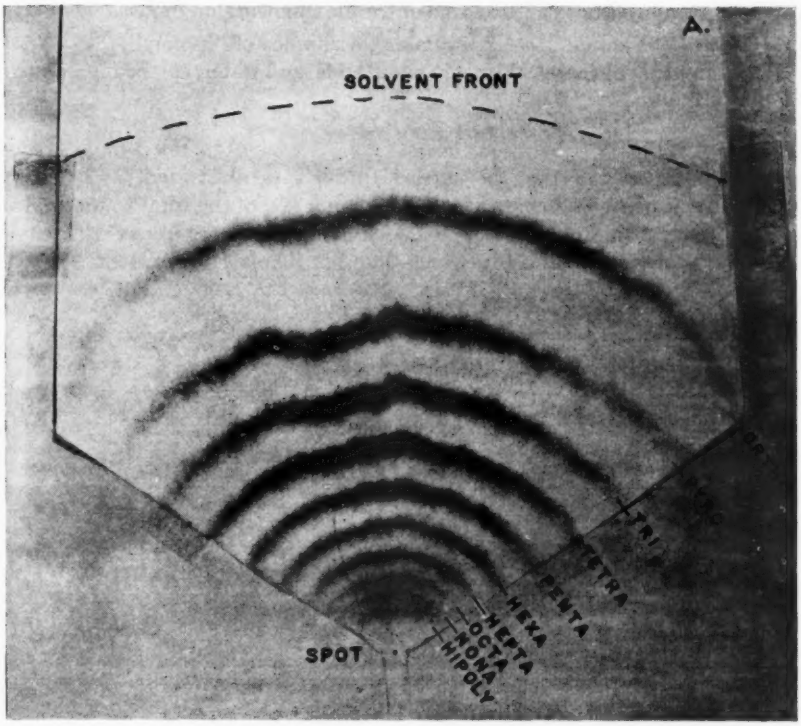

FIG. 4. Chromatographic separation of strong phosphoric acids.

Interpretation

This paper is concerned largely with presenting experimental results. Their interpretation in terms of chemical theory is a matter of much interest. Two methods are suggested by the current literature. First there is the method of Van Wazer (40) based on statistical models which is an application of modern polymer theory; secondly, there is the ionic and mass law method elaborated by Ingold and his school (20) in interpreting their cryoscopic measurements on sulphuric acid in the immediate neighborhood of the 100% sulphuric acid composition. Since the original derivation of the mass law by Guldberg and Waage was based on essentially a statistical argument, these two methods may not be as far apart as appears at first sight. In both cases, the strong phosphoric acids appear to be suitable materials for study.

ACKNOWLEDGMENT

The authors wish to thank Dr. A. E. R. Westman for his interest and help.

APPENDIX. COMPUTATION METHODS

The calculation of Table IV and the data for Fig. 3 from Table III is simple in principle, involving only stoichiometry and simple assumptions. Involved computations can be avoided by the following methods.

Free Water Content and Mole Percentages (in absence of "hypoly")

For computing purposes, the component acids, and water, can be represented by the formula

$$(H_2O)_{\frac{1}{2}(n+2)}(P_2O_5)_{\frac{1}{2}n}.$$

The computation can then be carried through as illustrated in Table V. Essentially, it involves a comparison, in Column (2), of the total water known to be present in the strong-acid mixture with that computed from the chromatographic analysis, Column (5), which does not include "free water".

TABLE V

(1) Over-all composition (wt. %)	(2)* H_2O	(3) Chromatographic analysis n	(4) Chromatographic analysis P_2O_5	(5) H_2O $(4)\times\frac{n+2}{n}$	(6) Components $(4)\times\frac{2}{n}$	(7) Components Mole %	(8) Moles HPO_3 per mole of H_2O $\frac{2}{(2)-1}$
		Moles per one mole P_2O_5 total					
		0			(2) 0.1248	6.4	
H_2O 27.56	2.9976	1	0.8728	2.6184	1.7456	87.4	1.0012
P_2O_5 72.44 (5)	2.8728	2	0.1272	0.2544	0.1272	6.4	
	0.1248		1.0000	2.8728	1.9876	100.0	

**Transferred values have the column of origin indicated in front.*

TABLE VI

(1) Over-all composition (wt. %)	(2)* H_2O	(3) Chromatographic analysis n	(4) Chromatographic analysis P_2O_5	(5) Component acids $(4)\times\frac{2}{n}$	(6) Component acids $\left(\frac{(5)}{(5)\text{ total}}\times 100\right)$	(7) "Hypoly" $\frac{\bar{n}}{\frac{2y}{x-y}}$	(8) Over-all composition $\frac{2}{(2)-1}$
	Moles per one mole P_2O_5 total				(mole %)		(moles)
H_2O 15.80	1.4785	0					H_2O 1.000
P_2O_5 84.20 (4)+(5)	1.2501	1	0.0363	0.0726	15.17		HPO_3 4.179
x	0.2284	2	0.1060	0.1060	22.15		
(4) y	0.2016	3	0.1163	0.0775	16.20		
$x-y$	0.0268	4	0.1305	0.0653	13.65		
		5	0.1217	0.0487	10.18		
		6	0.0975	0.0325	6.79		
		7	0.0819	0.0234	4.89		
		8	0.0592	0.0148	3.09		
		9	0.0491	0.0109	2.28		
		Total	0.7984	0.4517			
		"Hypoly" y	0.2016	(2) 0.0268	5.60	15.0	
				0.4785	100.00		

**Transferred values have the column of origin indicated in front.*

Number Average Chain Length of "Hypoly" and Mole Percentages (in absence of "free water")

As illustrated in Table VI, the first part of the computation is the same as in Table V but the water, x, in the "hypoly" fraction is computed rather than "free water", which is assumed to be absent. The component acid formula can now be written $H_2O(HPO_3)_n$. Then, if x moles of water and y moles of P_2O_5 are present in the "hypoly" fraction, $2y$ moles of HPO_3 can be formed, leaving $x-y$ moles of "hypoly" acids. The number average chain length, i.e. the average number of HPO_3 groups per molecule, will then be $2y/(x-y)$.

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ON THE INFRARED ABSORPTION OF WATER AND HEAVY WATER IN CONDENSED STATES[1]

By Paul A. Giguère and K. B. Harvey

ABSTRACT

The infrared spectra (from 2 to 30 μ) of thin films of H_2O and D_2O were measured at various temperatures between 20° and −180°C. A strong absorption band due to the librational mode of the water molecule has its maximum around 710 cm.$^{-1}$ in the liquid. In ice it is shifted to 800 cm.$^{-1}$ at −15°C. and 850 cm.$^{-1}$ at −170°C. The corresponding D_2O bands show the normal isotope shift. Thin films of water pressed between silver chloride plates could not be crystallized even at liquid air temperature as confirmed by their spectra, which were almost identical with those of the liquid.

INTRODUCTION

Water is of considerable importance in infrared spectroscopy for, in addition to being practically omnipresent in nature, it absorbs very strongly over wide regions of the infrared, and it can attack or dissolve many of the salts used as optic materials. In fact the need for cancelling absorption by atmospheric water vapor was largely responsible for such developments as the double-beam and the vacuum spectrometers. On the theoretical side, infrared study of water in various physical states can contribute valuable information on such fundamental problems as the structure of ice, for instance. Whereas the infrared spectrum of the vapor has been studied extensively, the most extensively, no doubt, of all triatomic molecules, those of the condensed phases, although much simpler, are less well known. This is particularly true of the solid for which the only data available on the fundamental vibrations are from the classical work of Fox and Martin (14). These authors could not extend their measurements beyond 7.5 μ, the transmission limit of the fluorite plates which they used to hold the samples. Previously Cartwright (9) had scanned the long wave-length region where he had observed two very broad bands at about 20 μ and 60 μ arising from restricted rotation or "libration" (ν_R) and restricted translation (ν_T) of the water molecule. Existence of these intermolecular vibrations has been anticipated by Bernal (3, 4) and by Ellis (12).

Since then no systematic investigations of these two bands have been reported, at least not for the solid phase.* The early measurements of Rubens and Ladenburg (33) on liquid water were made actually with a soap film. Sohm (35) studied very thin films of liquid (1 micron) in the 15 to 25 μ region where she observed for the ν_R band a series of rounded maxima separated by 52 cm.$^{-1}$ in H_2O and 41 cm.$^{-1}$ in D_2O. This unusual feature must have resulted from interference as it could not be reproduced afterwards (27). More numerous than the infrared are the Raman investigations of liquid water and ice. A number of reviews have been published in the past, the most recent of which is that of Lecomte (21). For comparison, the existing data are

[1]*Manuscript received January 27, 1956.*
Contribution from the Department of Chemistry, Laval University, Quebec, Que.

*NOTE ADDED IN PROOF.—*In a very recent paper Ferriso and Hornig (J. Chem. Phys. 23: 1464. 1955) mention incidentally an intense band in the infrared spectrum of ice at 812 cm.$^{-1}$ (temperature not stated) from an unpublished thesis by F. P. Reding.*

TABLE I

PREVIOUS DATA ON THE INFRARED AND RAMAN SPECTRA OF ICE

			ν (cm.$^{-1}$)				T, °C.	Ref.
Infrared	160						−10°	9
			1530					
			1644	2222	3256	3790	−9°	14
Raman								
53.5	212				3360		*	32
					3090		−180°	36
					3135			
					3196		*	30, 31
					3321			
	205	601		2225	3126		0°	18
					3330			
	210				3156		0°	11
	213				3147			
52	260				3264		*	25
					3347			
	212						−4°	17

*Temperature not stated.

TABLE II

EXISTING DATA ON THE MOLECULAR SPECTRA OF LIQUID WATER

			ν (cm.$^{-1}$)				T, °C.	Ref.
Infrared		670					*	33
			1615	2130	3300		*	13
	160	500					*	9
						3790	23°	10
		650	1570				18°	35
			1645					
			1649	2146	3382		3°	14
			1646	2128	3395		19°	14
			1642	2092	3426		70°	14
		645		2110		3920	*	27
Raman								
					3200			
60	172	510	1645	2150	3435	3990	*	6
		780			3600			
			1654		3233		*	19
					3433			
					3224			
		550	1643		3436		*	8
		700			3625			
	175	500	1659	2135	3150	4023	12°	24
		740			3480			
					3330			
					3530		37°	24
					3670			
					3312			
					3494		67°	24
					3650			
	144	440	1627	2170	3219		28°	18
					3445			
	149	450	1629	2118	3222		88°	18
					3460			
	200		1656	2167	3440	4000	40°	11
					3260			
60	175	475			3426		*	25
		758			3610			

*Not stated; presumably room temperature.

listed in Tables I and II. A remarkable feature of the Raman spectra is the ν_2 band which seems to be missing in ice as well as in water vapor although it is present, but rather weak, in liquid water. The data on heavy water are quite scanty (Table III); in particular, nothing is available on D_2O ice.

TABLE III

PREVIOUS RESULTS ON THE SPECTRA OF HEAVY WATER (LIQUID)

	ν (cm.$^{-1}$)						T, °C.	Ref.
Infrared			1220	1620	2500		*	13
	170	360					*	9
			1220	1620	2500	2980	*	28
		500	1160 1210				19°	35
Raman								
	170	500	1207		2389 2509 2366		18°	2
	123 178				2500 2646		*	1
	190	375	1208	1600	2515	2965	50°	11
					2373			
60	176	375	1207		2539		*	25
					2670			

**Presumably room temperature.*

Our interest in that question stemmed from a spectroscopic study of the products from water vapor dissociated in the electric discharge (15, 16). Adequate knowledge of the absorption spectrum of ice was, obviously, a prerequisite. Because time was limited and our interest merely incidental only those tests were carried out which required no elaborate preparation nor special equipment. Further work would certainly be desirable, specially in the far infrared, to determine accurately the various frequencies in the acoustical branch of the molecular spectrum of ice. In that respect Raman spectra of single crystals appear more promising than an infrared study of thin, oriented films of ice.

EXPERIMENTAL

The problem of getting thin enough films of water (of the order of a few microns) between insoluble, infrared-transparent plates and at various fixed temperatures down to that of liquid air presented many experimental difficulties. To realize controlled physical conditions an evacuable absorption cell similar to that used for studying the products of dissociated water (16)— minus the discharge tube— was used. The film of water, or heavy water, was held on, or between, 25 mm. salt disks placed in a massive copper block forming the bottom of the coolant well. Kovar or Housekeeper's metal–glass

seals were found equally suitable, although their average life is rather short despite precautions to minimize the thermal shocks. Heat transfer between the salt windows and the holder was improved by a film of silicone grease in which some finely powdered silver had been dispersed. Alternatively, packing some silver powder tightly around the window gave a slightly better thermal contact but was more tedious. In addition the silver tended to sinter after a few months' use so that it became difficult to remove the salt disk. The temperature of the film was measured with a tiny copper–constantan thermocouple embedded in the salt window. With the absorption cell evacuated the lowest temperature thus attained was −187°C. with liquid nitrogen (−196°) in the coolant well. The spectrometer was a Perkin-Elmer, Model 12C, modified for double pass. A sodium chloride prism covered most of the region investigated, but occasionally lithium fluoride and cesium bromide prisms were necessary. The absorption cell was designed so as to fill almost completely the space between the two spectrometer housings. Thus absorption by atmospheric water vapor was reduced and, at the same time, the cell windows were less likely to fog from condensation.

Several techniques were employed successively in obtaining a suitable film of water. At first a drop of liquid was simply pressed between two polished silver chloride disks. However, this led to the peculiar result that essentially the same absorption spectra were obtained at all temperatures even down to that of liquid air, thereby confirming that no crystallization had occurred (Fig. 1).

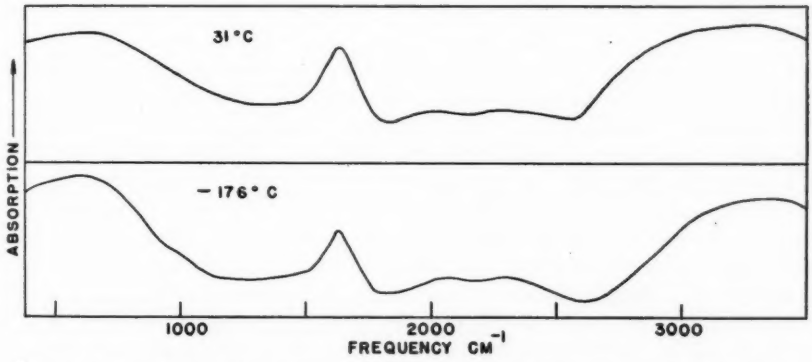

FIG. 1. Infrared absorption spectra of thin films of water between silver chloride plates.

This phenomenon could be repeated any number of times under the same conditions. Next, distillation *in vacuo* of a thin film from a liquid sample onto the salt disk cooled with liquid air was satisfactory at the lower temperatures (Fig. 2), but above −40°C. the infrared radiation of the spectrometer beam resulted in sublimation of the thin film followed by recondensation on the colder parts of the coolant well. Filling the cell with a dry gas did not improve the situation noticeably.

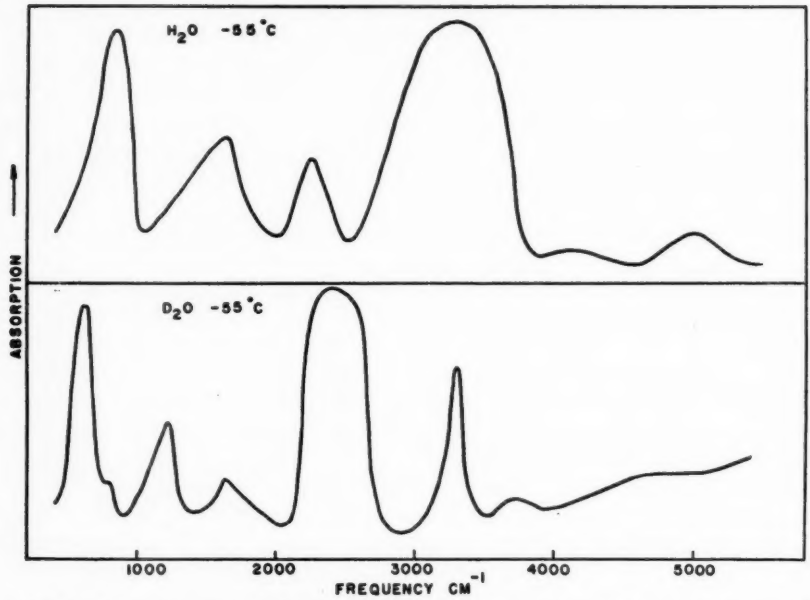

FIG. 2. Composite tracings of the infrared spectra of films of ice and heavy ice condensed on a plate at −55°C. (The weak band at 800 cm.$^{-1}$ and most of the sharp peak at 3300 cm.$^{-1}$ in the spectrum of D_2O ice are due to contamination by traces of H_2O.)

In an attempt to overcome this difficulty a third method was tried. After the film was formed by condensation, as above, the absorption cell was filled with dry gas and taken apart. Previously the coolant had been dumped out in order to prevent condensation of atmospheric water and carbon dioxide on the film. Then the latter was quickly covered with a second window separated by a thin gasket. Following reassembly the cell was evacuated again and the spectra recorded at various temperatures from that of liquid air up. By this stratagem evaporation was prevented but other complications ensued. For instance, the spectra showed considerable scattering at short wavelengths (Fig. 3) owing, no doubt, to coalescence of the microcrystals into larger ones when the film was warmed (temperature not measured but estimated in the order of −40° to −30°C.). That this phenomenon persisted above the melting point of ice is attributed to the formation of minute droplets of water on the non-wetted silver chloride plates.

In the case of heavy water still a different technique had to be developed because the ν_R band in the liquid state extends appreciably beyond 25 μ, the usable limit of silver chloride optics. The sample was placed between two thin sheets of polythene stretched across a cesium bromide window in a demountable liquid cell. Except for lack of rigidity this plastic, in thin sheets, is an excellent material for the 25–35 μ region.

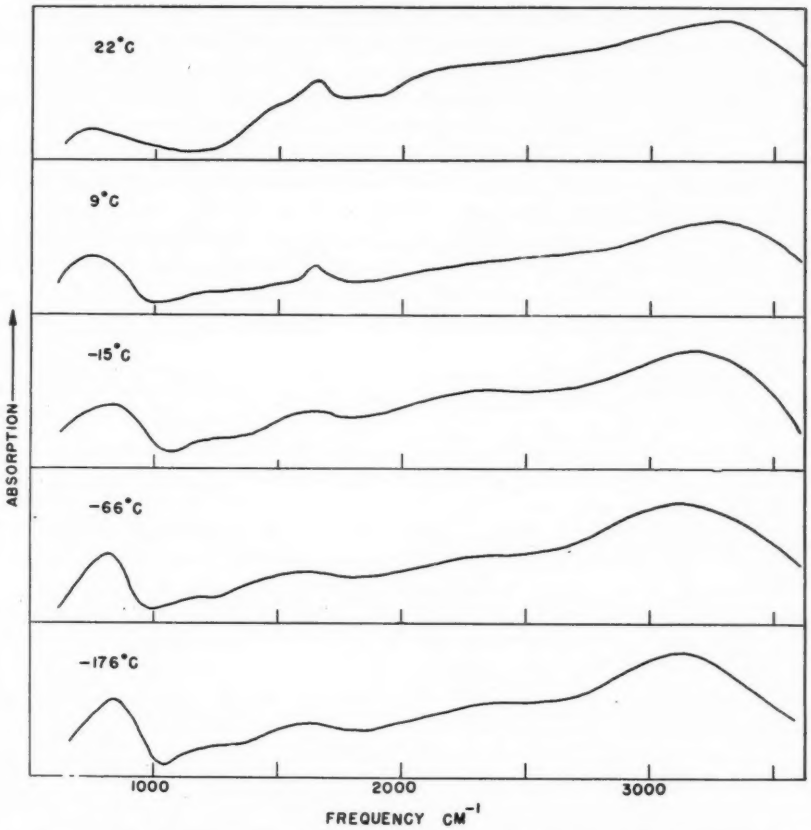

FIG. 3. Effect of temperature on the absorption spectra of thin films of ice condensed on a cold plate.

DISCUSSION OF RESULTS

The new results can best be considered from the two main viewpoints of librational frequency and supercooling of water.

The Librational Frequency

Heretofore the frequency of ν_R in water was not known with any great accuracy owing, mostly, to the flatness and width of the band. Values ranging from 450 to 780 cm.$^{-1}$ (cf. Table II) have been reported for the liquid phase. Some of these estimates were based in part on the frequency of the combination tone, $\nu_2+\nu_R$, at about 2200 cm.$^{-1}$. However, there was a tendency to underestimate the extent of anharmonicity which is quite large, as expected, (some 200 cm.$^{-1}$) on account of the strong interaction of these two deformation modes. The present value, 710 cm.$^{-1}$ is believed correct to $\pm$10 cm.$^{-1}$ on the

basis of the tracings obtained with the third technique; that is, where the liquid sample was *not* pressed between two salt plates. Indeed, it was observed repeatedly in this work that the ν_R band of compressed films of water was appreciably broader than that of films deposited on a plate. Plyler and Acquista (27) using a film estimated as 0.005 mm. thick have observed an extremely broad band extending from 12 to 40 μ.

As could be surmised, the frequency of ν_R in water is strongly dependent on temperature and physical state. Thus on crystallization it is shifted by about 90 cm.$^{-1}$ towards the shorter wavelengths and the temperature coefficient in ice is fairly large (Table IV). Fox and Martin (14) had found a shift

TABLE IV

PRESENT DATA ON THE INFRARED BANDS OF H_2O AND D_2O IN CONDENSED STATES

Mode	Int.	H_2O				D_2O			
		Liquid 10°	Crystal			Liquid 10°	Crystal		
			−15°	−55°	−170°		−15°	−55°	−170°
ν_R	s.	710	800	820	850	530	590	610	630
$2\nu_R$	v.w.			1500					
ν_2	m.			1650	1650			1210	1210
$\nu_2+\nu_R$	m.			2240	2250			1620	1630
ν_3	v.s.			3240	3260			2440	2450
	v.w.			4150				3295	
	v.w.			5000				3720	

of 75 cm.$^{-1}$ for the combination band $\nu_2+\nu_R$ in fair agreement with our observation since the frequency of ν_2 is little affected by changes of phase. This increase of about 13% in the force constant of ν_R upon crystallization follows from a tightening of the hydrogen bonds (shortening of the O–H . . . O distance). It may be recalled here that Pauling (26) has estimated that 15% of the hydrogen bonds in ice are broken on melting. There are indications in the Raman spectra (Tables I and II) that the other lattice vibration ν_T has a slightly higher frequency in ice than in water.

The value of ν_R in ice is of interest in connection with various physical properties such as specific heat and zero-point energy of the lattice. Twenty years ago Bernal and Tamm (4) calculated the librational frequency from the ice model of Bernal and Fowler (3) and thus arrived at a much lower result, 475 cm.$^{-1}$. From this they estimated the difference of the heats of vaporization of H_2O and D_2O ices to be 0.35 kcal./mole at the melting points. This is now known to be 0.46 kcal./mole (20), not 0.32 as was then believed on the basis of extrapolated data for the vapor pressure of D_2O (22). More recently Blue (5) has calculated an approximate value of ν_R in the temperature region below the melting point. His method, which rests on the difference between the measured heat capacity of ice and heavy ice, also leads to a somewhat lower result than ours, namely 660 cm.$^{-1}$ (723 cm.$^{-1}$ when hindered translation is

taken into account).* From an analysis of the three modes of libration around each of the principal axes of the molecule Blue has concluded that the three frequencies should differ among themselves by less than 10% for ice and less than 20% for heavy ice. Another conclusion from his analysis is that the librational frequencies decrease with rising temperature. Our results do show an appreciable decrease in frequency. It is doubtful, however, if the effect becomes much larger near the melting point of ice.

Although they did not attempt to locate the maximum of the broad, flat ν_R bands in the Raman spectra of H_2O and D_2O, Cross *et al.* (11) deduced from their analysis of the structure of ice that it should have a frequency of the order of 700 to 900 cm.$^{-1}$. The present figure, exactly halfway in that range, is further evidence for the soundness of their perturbation treatment of the water molecule.

The Supercooling of Water

The persistence of the liquid-type absorption spectra of thin films of water down to liquid-air temperature (Fig. 1) was unexpected. The frequency of ν_R provided a reliable criterion for this, as the other bands are either too broad or little affected by phase changes. Previous instances have been reported of thin films of water in a non-crystalline state at very low temperatures (7, 23, 29). In all these cases, however, the samples were cooled very quickly and they usually crystallized on being warmed above a certain temperature. Our films of water pressed between silver chloride plates could be warmed and cooled over a wide temperature range without significant alteration in their spectra. Fox and Martin (14) obtained crystalline films of ice at −9°C. by "jolting" the absorption cell. We confirmed that thin films of water between fluorite plates become rigid quite readily around −10° simply by moving one plate with respect to the other. Our experimental arrangement did not make this test possible at liquid air temperature but on the other hand jolting or tapping the sample holder never induced crystallization at that temperature. The difference, no doubt, comes from the fact that under such conditions our samples were well below the temperature range of maximum rate of nucleation in supercooled water.

The recent work of Pryde and Jones (29) has thrown new light on the low-temperature forms of water-substance. In particular they have confirmed the observations of Simon (34) that vitreous (or glassy) water has an appreciably smaller heat capacity than supercooled water (Fig. 4) and in one experiment they were able to follow the reversible transition, near −147°C. (T_g), in a finely subdivided sample of water held in a porous copper block. On the other

**Some of the Raman data quoted by this author in comparison with his calculated results were misinterpreted. The "strong sharp line at about 600 cm.$^{-1}$" in the spectra published by Cross, Burnham, and Leighton (11) was not identified by them with the librational motion. In fact this band is much too sharp for an O–H vibration in condensed phases. Furthermore, it appears unchanged in the Raman spectra of both liquid* and *solid* H_2O and D_2O *(Figs. 2 and 3 of Ref. 11). Undoubtedly it was due to an unfiltered line in the mercury–argon discharge used for that work, presumably the 2576.29 Å line arising from the* $6s6p^3P_1$–$6s9s^3S_1$ *transition of the mercury atom. (Private communication from Prof. Leighton.) The same phenomenon may have occurred in Hibben's work (18), although there the situation is not so clear.*

hand the material formed by condensation from the vapor into calorimeters cooled in liquid oxygen, although it appeared transparent, was only partly vitreous because it always crystallized irreversibly at a fixed temperature, 129°±1°C. From the heat evolved the vitreous fraction was estimated to range from one-twentieth to one-third, depending on the thickness and the rate of formation of the layers.

The present results seem to fit well into that picture. Indeed, the thin films condensed from water vapor did look glassy at liquid air-temperature but they turned snowy white in the vicinity of −120°C. That the infrared spectrum remained unchanged thereupon (Fig. 3) may be due to either or both of the following causes: (*a*) the films were largely crystalline to begin with or (*b*) the absorption spectrum of vitreous water is similar to that of ice but different from that of the supercooled liquid. The latter view appears logical considering the large contribution of intermolecular vibrations to the heat capacity of condensed phases (Fig. 4). In the X-ray experiments of Burton and Oliver (7)

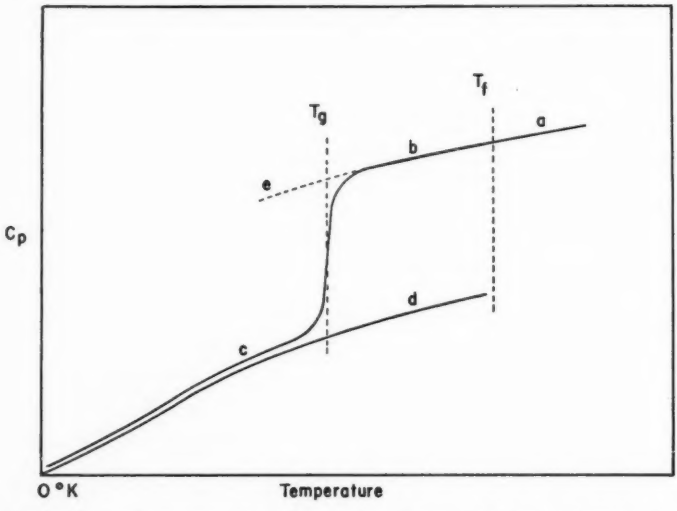

FIG. 4. Specific heat – temperature curves, after Simon (34), for a substance in the following states: (*a*) liquid, (*b*) supercooled liquid, (*c*) glass, (*d*) crystal, and (*e*) equilibrium curve for supercooled liquid.

water vapor condensed on surfaces colder than −110° was found to be vitreous while above −80° ice was obtained. Between these two temperatures crystallization would take place only along certain crystallographic planes. Since their samples were prepared extremely slowly and at very low pressures (10^{-4} mm. Hg) the heat of condensation was quickly dissipated, an essential condition for glass formation. Our attempts to repeat their experiments were unsuccessful (the films were in all cases crystalline) presumably because evaporation was carried out at a much higher pressure (5×10^{-2} mm. Hg).

Another factor may be that silver chloride is a poorer heat conductor than metallic copper used by Burton and Oliver for holding their samples.

No estimate of the absorption coefficients of the various bands will be attempted here since the thickness of the films was not measured. The matter is further complicated by the scattering and broadening phenomena mentioned above. Qualitatively speaking the intensity of the 6 μ band in ice decreases on cooling while that of the 3 μ band increases (Fig. 3). The same trend had already been noticed in liquid water (14). From Fig. 1 it seems that this effect is much less pronounced in the vitreous state. As for the ν_R band, it is not only sharper, but also stronger in ice than in liquid water.

ACKNOWLEDGMENT

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RÉSUMÉ

On a mesuré l'absorption infrarouge (de 2 à 30 μ) de l'eau ordinaire et de l'eau lourde dans les états liquide et solide. La libration, ou rotation gênée des molécules, donne naissance à une forte bande d'absorption aux environs de 710 cm.$^{-1}$ dans l'eau liquide. Dans la glace cette bande se retrouve vers 800 cm.$^{-1}$ au voisinage du point de fusion et vers 850 cm.$^{-1}$ à la température de l'air liquide. Les fréquences correspondantes dans l'eau lourde sont à 530, 590 et 630 cm.$^{-1}$. On a constaté que dans le cas de minces films d'eau retenus entre deux plaques polies de chlorure d'argent le spectre demeure essentiellement le même lorsqu'on refroidit jusqu'à -180°C., ce qui indiquerait l'absence de cristallisation.

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THE DETERMINATION OF PARTIAL SPECIFIC VOLUMES BY DIFFERENTIAL SEDIMENTATION[1]

By W. G. Martin, W. H. Cook, and C. A. Winkler[2]

ABSTRACT

Sedimentation in aqueous and heavy water solutions has been used to determine the partial specific volume of bovine plasma albumin, sodium alginate, and polyvinyl alcohol, resulting in 0.74 ± 0.01 (S.D.), 0.54 ± 0.06, and 0.79 ± 0.01 ml./gm. at 25°C., respectively. The sedimentation method yields results comparable with those given by conventional methods for macromolecules.

INTRODUCTION

The estimation of molecular weight by sedimentation requires a knowledge of the partial specific volume of the sedimenting material. With purified protein preparations a satisfactory value of the partial specific volume, $\bar{V}$, can often be assumed from published results. However this is not possible for macromolecules that have not been extensively studied. The classical pycnometer (19) and float (6) methods require more material than may be available and the density gradient column (11) has limitations when applied to such materials as lipoproteins.

McBain (14) postulated that $\bar{V}$ of macromolecules could be estimated from their differential sedimentation rate in media of differing density. Obviously such estimates will be subject to the combined errors of at least two sedimentation determinations and these will be in general greater than the errors applicable to the classical methods of determining density. The classical methods, however, are far more sensitive than the sedimentation method to errors in concentration or residual hydration and small percentages of impurities. Such errors are inevitable with macromolecules that have a great affinity for water, decompose at elevated temperatures, or associate with other substances. The sedimentation method is attractive, therefore, since it is less subject to the errors often inherent in the material itself and since it requires only a small sample.

Evaluation of $\bar{V}$ of macromolecules by the sedimentation method has been made from experiments in which glycerol, sucrose, serum albumin, or deuterium oxide (4, 12, 13) was used to vary the density of the sedimentation medium. Although the range of density obtainable with deuterium oxide is limited, it can be assumed to behave in the same manner as water and thus avoids the uncertainties of differential interaction between solvent and solute inherent in the use of other materials. With the exception of polystyrene latex spheres, previous experiments with deuterium oxide were made on materials of uncertain physical characteristics.

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In the present study sodium alginate (AC_1), bovine plasma albumin (BPA), and polyvinyl alcohol (PVA) were selected as a typical polyelectrolyte, globular protein, and linear polymer, respectively, and their sedimentation rates in aqueous and heavy water media were measured.

THEORY

From the theory of particle sedimentation in high centrifugal fields, Svedberg (19) developed the relation:

$$[1] \qquad fs = M(1-\bar{V}\rho)$$

where f, s, M, and $\bar{V}$ are respectively the frictional coefficient, sedimentation coefficient, molecular weight, and partial specific volume of the macromolecule and ρ is the density of the sedimentation medium.

The frictional coefficient f in equation [1] is obviously a function of the shape and effective volume of the molecule in solution and also of the viscosity of the solvent. Corrections can be made for viscosity differences, to permit the use of a frictional coefficient independent of solvent viscosity defined by the equation:

$$[2] \qquad f = f'\eta.$$

It is reasonable to assume that there will be no significant differences in molecular shape and effective volume of macromolecules in aqueous and heavy water media (18). Again little effect upon electrostriction would be expected. However, a significant and rapid exchange of deuterium atoms for labile hydrogen atoms (10, 17) of macromolecules will occur in solutions containing deuterium oxide. The result will be an increase in molecular weight and since the volume of the macromolecules does not change, $\bar{V}$ will decrease. Thus M in aqueous solution will become Mk in deuterium oxide and $\bar{V}$ will change to $\bar{V}/k$, where k is the ratio of the molecular weights in the two media. Some preliminary measurements of $\bar{V}$ in aqueous and heavy water solutions indicated that $\bar{V}$ was lower in the latter solvent (15).

The sedimentation in aqueous and heavy water solutions may therefore be expressed as:

$$[3] \qquad f'\eta_1 s_1 = M(1-\bar{V}\rho_1),$$

$$[4] \qquad f'\eta_2 s_2 = Mk(1-\bar{V}\rho_2/k).$$

Dividing equation [3] by equation [4] and rearranging,

$$[5] \qquad \bar{V} = (\eta_2/\eta_1 - k\, s_1/s_2)(\rho_1\eta_2/\eta_1 - \rho_2 s_1/s_2)^{-1}.$$

The standard error of $\bar{V}$ can be approximated from the observed standard errors of s_1 and s_2 by the conventional device of regarding mathematical differentials as statistical differentials. Partial differentiation of equation [5] results in:

$$[6] \qquad \partial\bar{V}/\partial s_i = Fs_j$$

where $i = 1$ when $j = 2$ and vice versa, and where $F = (k\rho_1 - \rho_2)\eta_1\eta_2/(\rho_1 s_2\eta_2 - \rho_2 s_1\eta_1)$. Now assuming that η and ρ have negligible errors, that s_1 and

s_2 have the same small proportional error, and that the joint fractional error of s_1 and s_2 is the root-sum-square of the individual errors, equation [6] can be transformed to give:

$$[7] \qquad \Delta\bar{V} = F(s_1^2\Delta^2 s_2 + s_2^2\Delta^2 s_1)^{\frac{1}{2}}$$

where Δ is to be read "the standard error of".

EXPERIMENTAL

Material

Crystalline BPA (Armour) was used without further purification. The PVA (Shawinigan Chemicals Ltd.) and AC_1 (Alginate Industries Ltd.) were dissolved in distilled water, filtered or centrifuged to remove any insoluble material, and then lyophilized. Weighed amounts of AC_1 were redissolved in measured volumes of buffer solution and again lyophilized. Each material was stored over P_2O_5 *in vacuo*.

The BPA and PVA were caused to sediment in 0.2 μ sodium chloride solution and dilutions were made by adding solvent to a stock solution. Known weights of the lyophilized AC_1 were dissolved in the calculated weight of solvent and sedimentation was in 0.15 μ sodium phosphate – sodium chloride buffer at pH 6.6. Some solutions of each material were made directly by weight.

Methods

The densities of the heavy water and heavy water solutions were measured mainly in the density gradient column at 25°C. Some of the measurements on the heavy water and all of the density measurements of the aqueous solutions were made with a small magnetic float (15). The stock solution of deuterium oxide had a density of 1.039 gm./ml. but that used for making the solutions following storage in secondary stock bottles varied from 1.035 to 1.039 gm./ml.

The viscosity of the deuterium oxide as determined in an Ostwald-Fenske viscometer was 1.099 centipoise at 25.0°C. Viscosities of the salt solutions were obtained from the solvent viscosities plus the increments due to the salts, calculated from Svedberg's tables (19).

Sedimentation experiments were made with the Spinco ultracentrifuge in a 12 mm. cell at 59,780 or 52,640 r.p.m. with a few experiments at lower concentrations in a 30 mm. cell at 50,740 r.p.m. The intercepts at zero concentration in aqueous medium for AC_1 and BPA were calculated from published data (5, 16, 21). The data were corrected for the drop in rotor temperature with acceleration (2, 22) unless, as in some experiments, the temperature was controlled by a rotor temperature indicator and control unit. The experiments were made at approximately 25°C. and the sedimentation coefficients were corrected to 25°C. by multiplying by η_t/η_{25}, where η refers to the viscosity of the sedimentation medium (1).

The accepted values of $\bar{V}$ for BPA and PVA were taken from the literature (6, 7, 8, 20) but the value for AC_1 was redetermined with a float apparatus similar to that of MacInnes (6). For this determination the refractive index increment of sodium alginate (5) of 152×10^{-5} gm.$^{-1}$ dl.$^{-1}$ was used to estimate concentration.

RESULTS AND DISCUSSION

Extrapolation of the experimental data to zero concentration minimizes errors arising from concentration dependence and hydration and enables the solvent viscosity to be used in correcting to standard conditions. The $S^{\circ}_{25,\ \text{medium}}$ values were calculated from the intercepts of Fig. 1. The relation

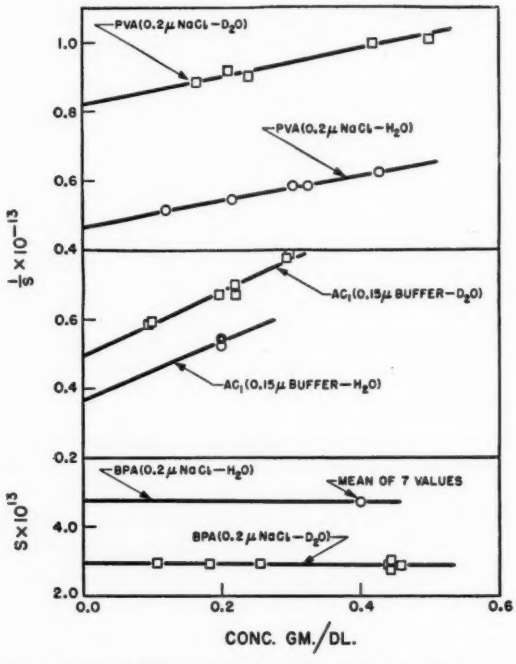

FIG. 1. Concentration dependence of the sedimentation coefficients of bovine plasma albumin, sodium alginate, and polyvinyl alcohol, in aqueous and heavy water media at 25°C.

between sedimentation coefficient and concentration was linear for BPA but a plot of $1/S$ vs. C was necessary to obtain a linear relation for PVA and AC_1. The lines in Fig. 1 were fitted by the method of least squares.

The results are summarized in Table I. The reported $\bar{V}$ values were computed by equation [5]. From the amino acid composition of BPA (9), the number of labile hydrogen atoms was estimated, and k was calculated. Similarly the number of labile hydrogen atoms in each repeating unit of AC_1 (3) and PVA (8) was used to calculate k for these macromolecules.

The value of 0.74 ± 0.01 (S.D.) for $\bar{V}$ of BPA is satisfactory, as it shows a small random error and is in good agreement with the value of 0.734_3 determined with MacInnes float equipment (6).

The partial specific volume of 0.54 ± 0.06 found for AC_1 shows a relatively high experimental error and is considerably higher than the value of 0.481 ± 0.003 obtained at four concentrations with the MacInnes apparatus in this

TABLE I

DATA AND CALCULATION OF $\bar{V}$

	BPA in 0.2 μ NaCl		AC_1 in 0.15 μ buffer		PVA in 0.2 μ NaCl	
	H_2O	D_2O	H_2O	D_2O	H_2O	D_2O
S°_{25}, medium, svedberg units	4.78±0.04	2.97±0.03	2.76±0.06	2.02±0.05	2.14±0.03	1.22±0.03
η_{25}, medium, cp.	0.912	1.117	0.919	1.124	0.912	1.117
ρ_{25}, medium, gm./ml.	1.005	1.112	1.004	1.111	1.005	1.113
k		1.016		1.011		1.023
$\bar{V}$ (equation [5]), ml./gm.	0.74±0.01		0.54±0.06		0.79±0.01	
$\bar{V}$ (conventional methods)	0.734₂ (6)		0.481±0.003		0.765 (8) 0.748±0.005 (7) 0.762±0.003 (20)	

investigation. However, the latter value may be subject to somewhat greater total error since the concentration was determined from the refractive index increment. An error of 1% in estimating concentration could result in an error in $\bar{V}$ of 0.005. Considering the magnitude of the random and possibly bias errors, the difference in $\bar{V}$ might not be important.

From the literature, $\bar{V}$ of PVA was 0.765 (8), 0.748±0.005 at 25°C. (7), and 0.762±0.003 at 25°C. (20). The value of 0.79±0.01 at 25°C. by the sedimentation method is high, but does not differ significantly from the other values.

Thus, $\bar{V}$ of the macromolecules obtained by sedimentation in aqueous and heavy water media is comparable with $\bar{V}$ obtained by classical methods. The sedimentation method would be especially useful for material in short supply, of uncertain concentration, or both.

ACKNOWLEDGMENT

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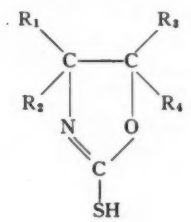
THE STRUCTURES AND CHEMISTRY OF THE PRODUCTS FROM THE REACTION OF AMINO ALCOHOLS WITH CARBON DISULPHIDE[1]

By M. Skulski, D. L. Garmaise, and A. F. McKay

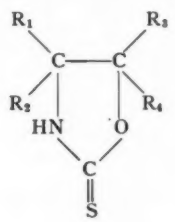
ABSTRACT

A study of the infrared spectra of the oxazoline derivatives, which are formed by the condensation of carbon disulphide with amino alcohols, shows that they possess the oxazolidine-2-thione structure rather than the tautomeric 2-thiol-2-oxazoline structure. 2-Benzylamino-4,4-dimethyl-2-oxazoline was formed by the reaction of benzylamine with 2-methylmercapto-4,4-dimethyl-2-oxazolinium iodide. 5-Diethylaminomethyl-2-oxazolidone and its methylation product also have been prepared.

The structures of the oxygen–nitrogen containing heterocyclics from the reaction of carbon disulphide with amino alcohols have been described previously as either oxazoline-2-thiols (I) (2, 8) or oxazolidine-2-thiones (II) (4, 5). Structure I is encountered most frequently in the literature (8) although Ettlinger (3) describes the infrared spectra of oxazolidine-2-thione and 5,5-dimethyloxazolidine-2-thione in detail. A further study of the infrared spectra



I



II

(Table I) of several of these heterocyclics and their corresponding methylation products confirms structure II as the correct one for these condensation

TABLE I

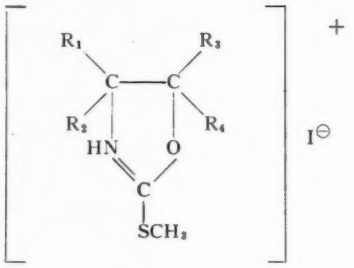
INFRARED ABSORPTION BAND OF SUBSTITUTED OXAZOLIDINE-2-THIONES

Compound	N—H stretching	C=N	N—H bending
4-Methyl-4-hydroxymethyloxazolidine-2-thione	3380[a]		1526
	3265[a]		
	3145		
4,4-Dimethyloxazolidine-2-thione	3155		1525
5-Diethylaminomethyloxazolidine-2-thione	3140		1546
2-Methylmercapto-4,4-dimethyl-2-oxazolinium iodide	3275	1646	1533
	3030		
2-Methylmercapto-4-ethyl-2-oxazolinium iodide	3315	1641	1528

[a]*One of these bands may be the result of O—H stretching vibrations.*

[1]*Manuscript received February 3, 1956.*
Contribution from the L. G. Ryan Research Laboratories of Monsanto Canada Limited, Ville LaSalle, Quebec.

products. The infrared spectra of 4-methyl-4-hydroxymethyloxazolidine-2-thione (II, $R_1 = CH_3$; $R_2 = HOCH_2$; R_3 and $R_4 = H$), 4,4-dimethyloxazolidine-2-thione (II, R_1 and $R_2 = CH_3$; R_3 and $R_4 = H$), and 5-diethylaminomethyloxazolidine-2-thione (II, R_1, R_2, and $R_3 = H$; R_4 = diethylaminomethyl) show the absence of a C=N band and the presence of strong N—H stretching and bending bands. On the other hand 2-methylmercapto-4,4-dimethyl-2-oxazolinium iodide (III, R_1 and $R_2 = CH_3$; R_3 and $R_4 = H$) and 2-methylmercapto-4-ethyl-2-oxazolinium iodide (III, R_1, R_3, and $R_4 = H$; $R_2 = C_2H_5$) do have strong C=N stretching bands at 1646 cm.$^{-1}$ and 1641 cm.$^{-1}$ respectively in agreement with their structure (III).



III

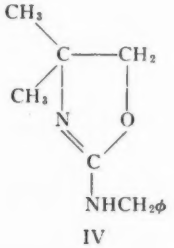
The yields of the substituted oxazolidine-2-thiones with the exception of 4-methyl-4-hydroxymethyloxazolidine-2-thione are based on the following equation:

$$2NH_2CR_1R_2CR_3R_4OH + CS_2 \rightarrow HOCR_3R_4CR_1R_2NHCS_2^{\ominus}\overset{\oplus}{N}H_3CR_1R_2CR_3R_4OH$$

$$\xrightarrow{\Delta^-} II + NH_2CR_1R_2CR_3R_4OH + H_2S.$$

The yield of 4-methyl-4-hydroxymethyloxazolidine-2-thione was raised to 84.7% (based on conversion of 1 mole equivalent of amino alcohol into 1 mole equivalent of the substituted oxazolidine-2-thione) by intermittent refluxing of the reaction mixture with additional portions of carbon disulphide.

2-Methylmercapto-4,4-dimethyl-2-oxazolinium iodide was converted into 2-benzylamino-4,4-dimethyl-2-oxazoline (IV) by refluxing with benzylamine in the presence of ethanol. This reaction is similar to the conversion of 2-



IV

methylmercapto-2-imidazolines into 2-substituted amino-2-imidazolines previously (1, 7) described.

During the course of this work 5-diethylaminomethyl-2-oxazolidone (m.p. 51.5–53°C.) and 5-(diethyl methyl ammonium methyl)-2-oxazolidone iodide (m.p. 160.5–161.5°C.) also were prepared.

EXPERIMENTAL[2]

4,4-Dimethyloxazolidine-2-thione (*6*, *8*)

2-Amino-2-methyl-1-propanol (44.6 gm., 0.5 mole) in benzene (150 cc.) was added dropwise to a stirred solution of carbon disulphide (35.3 gm., 0.55 mole) in benzene (150 cc.) at 5°C. over a period of 15 min. The stirring was continued for 30 min. at room temperature after which the yellow crystalline intermediate was recovered by filtration. This dithiocarbamate salt was heated in an oil bath at 105–135°C. until the evolution of hydrogen sulphide ceased. The cooled residue was triturated with water (100 cc.) and the colorless crystals (m.p. 121–123°C.) were removed by filtration, yield 24.7 gm. (75.3%). Two crystallizations from water raised the melting point to 123.5–124°C. Calc. for C_5H_9NOS: C, 45.77; H, 6.91; N, 10.68%. Found: C, 45.58; H, 6.60; N, 10.3%.

2-Methylmercapto-4,4-dimethyl-2-oxazolinium Iodide

4,4-Dimethyloxazolidine-2-thione (20 gm., 0.15 mole) was refluxed in a solution of methyl iodide (23.8 gm., 0.16 mole) in absolute methanol (70 cc.) for 30 min. On cooling in a freezing mixture, colorless crystals (m.p. 80–82°C.) were obtained, yield 25.2 gm. (57.3%). The melting point was raised to a constant value of 84–85°C. by one crystallization from cold absolute methanol. Calc. for $C_6H_{12}INOS$: C, 26.38; H, 4.43; S, 11.74; N, 5.13%. Found: C, 26.67; H, 4.15; S, 11.45; N, 4.94%.

2-Benzylamino-4,4-dimethyl-2-oxazoline

A solution of 2-methylmercapto-4,4-dimethyl-2-oxazolinium iodide (25.15 gm., 0.09 mole) and benzylamine (9.87 gm., 0.09 mole) in ethanol (10 cc.) was refluxed for eight and a half hours. Removal of the ethanol *in vacuo* under an atmosphere of nitrogen gave a turbid oil (yield 30 gm.). A small sample of this oil was converted into its picrate (m.p. 149–150°C.) in the usual manner. Two crystallizations from ethanol raised the melting point to 150–151°C. Calc. for $C_{18}H_{19}N_5O_8$: C, 49.86; H, 4.42; N, 16.15%. Found: C, 49.54; H, 4.39; N, 16.3%.

The major portion (27.76 gm.) of the oily reaction product was dissolved in warm (50°C.) water (500 cc.) and the solution was passed through a column of Amberlite IRA-400 resin (300 cc.) at a rate of 7–8 cc. per min. The column was washed with 8500 cc. of water. Colorless needles (m.p. 73–73.5°C.) were obtained in 55.5% yield (11.5 gm.) from the effluent and washings on evapora-

[2] *All melting points are uncorrected. Microanalyses were determined by Micro-Tech Laboratories, Skokie, Illinois, and Drs. G. Weiler and F. B. Strauss, Oxford, England.*

tion *in vacuo* under nitrogen. Two crystallizations from carbon tetrachloride raised the melting point of the 2-benzylamino-4,4-dimethyl-2-oxazoline to 79–80.5°C. Calc. for $C_{12}H_{16}N_2O$: C, 70.53; H, 7.89; N, 13.72%. Found: C, 70.81; H, 7.83; N, 13.78%.

4-Ethyloxazolidine-2-thione

4-Ethyloxazolidine-2-thione (m.p. 73–74°C.) (8) was prepared from 2-amino-1-butanol by the method described above for 4,4-dimethyloxazolidine-2-thione. Calc. for C_5H_9NOS: C, 45.77; H, 6.92; N, 10.68; S, 24.44%. Found: C, 45.92; H, 6.47; N, 10.5; S, 24.8%.

2-Methylmercapto-4-ethyl-2-oxazolinium Iodide

A solution of 4-ethyloxazolidine-2-thione (4 gm., 0.03 mole) and methyl iodide (4.33 gm., 0.03 mole) in 35 cc. of absolute methanol was refluxed for 30 min. The residue, after removal of the methanol *in vacuo*, crystallized on standing, yield 3.91 gm. (43.4%). Crystallization from absolute methanol raised the melting point from 83–84.5°C. to 84.5–85.5°C. Calc. for $C_6H_{12}INOS$: C, 26.38; H, 4.43; N, 5.13%. Found: C, 26.27; H, 4.44; N, 5.12%.

4-Methyl-4-hydroxymethyloxazolidine-2-thione

Carbon disulphide (83.75 gm., 1.1 mole) was added to a stirred solution of 2-amino-2-methyl-1,3-propanediol (105.1 gm., 1 mole) in ethanol (750 cc.) at 2–5°C. over a period of 25 min. This solution was refluxed for six hours after which a second portion of carbon disulphide (42 gm., 0.55 mole) was added and the refluxing continued for another 16 hr. Finally a third portion (80 gm., 1.05 moles) of carbon disulphide was added and the solution was refluxed for a further 16 hr. After removal of the excess carbon disulphide and solvent, a brown semicrystalline residue was obtained. It was triturated with acetone and the colorless crystals (m.p. 88–93°C.) were removed by filtration, yield 124.5 gm. (84.7%). The crude material was purified to a constant melting point of 92.5–93.5°C. by several crystallizations from ethyl acetate. Calc. for $C_5H_9NO_2S$: C, 40.79; H, 6.16; N, 9.52; S, 21.79%. Found: C, 40.95; H, 6.73; N, 9.65; S, 21.6%.

A portion (19.5 gm., 0.13 mole) of the 4-methyl-4-hydroxymethyloxazolidine-2-thione was refluxed in absolute methanol (75 cc.) with methyl iodide (20.7 gm., 0.146 mole) for 30 min. Removal of the alcohol *in vacuo* under nitrogen gave a yellow crystalline product (m.p. 112–114.5°C.), yield 13.76 gm. (79.2%). Crystallization from ethyl acetate raised the melting point to 115.5–116.5°C. This material gave a negative qualitative test for sulphur and its analytical values agreed with those calculated for 4-methyl-4-hydroxymethyl-2-oxazolidone. Homeyer (5) reported the melting point of this compound as 115–116.5°C. Calc. for $C_5H_9NO_3$: C, 45.80; H, 6.92%. Found: C, 45.68; H, 6.74%.

5-Diethylaminomethyloxazolidine-2-thione

A solution of 1-amino-3-diethylamino-2-propanol (219.4 gm., 1.5 moles)

in 1000 cc. of benzene was added dropwise to a stirred solution of carbon disulphide (125.6 gm., 1.65 moles) in 1750 cc. benzene at 2°C. over a period of four hours. After 15 min., a grayish precipitate formed. The reaction mixture was allowed to stand overnight in the refrigerator after which the solid material was removed by filtration. This solid was suspended in 3000 cc. of ethanol and the solution was refluxed until the evolution of hydrogen sulphide ceased. The resulting brown ethanol solution was filtered to remove sulphur and then treated with Norite A. The filtrate, on evaporation to one-third its original volume and cooling, gave colorless needles. A second crop was obtained from the mother liquor. The total yield of crude product (m.p. 95–97°C.) was 109 gm. (77.2%). This crude material after crystallization from ethanol melted at 96–97°C. Calc. for $C_8H_{16}N_2OS$: C, 51.02; H, 8.57; N, 14.86; S, 17.03%. Found: C, 51.15; H, 8.55; N, 14.70; S, 16.9%.

A picrate formed in the usual manner melted at 154–155°C., yield 77.2%. Calc. for $C_{14}H_{19}N_5O_8S$: C, 40.27; H, 4.58; N, 16.7%. Found: C, 40.33; H, 4.88; N, 16.6%.

A sample (2.8 gm., 0.015 mole) of 5-diethylaminomethyloxazolidine-2-thione in 9 cc. of methanol was treated with hydriodic acid (2.05 cc., $d = 1.7$). On addition of dry ether (150 cc.) to this solution, an oil separated. This oil crystallized (m.p. 113–120°C.) on standing, yield 4.23 gm. (90.0%). Two crystallizations from ethanol raised the melting point of the hydroiodide salt to 124–126°C. Calc. for $C_8H_{17}IN_2OS$: C, 30.39; H, 5.42; N, 8.86%. Found: C, 30.60; H, 5.60; N, 9.0%.

5-Diethylaminomethyl-2-oxazolidone

1-Amino-3-diethylamino-2-propanol (18.31 gm., 0.125 mole) and diethyl carbonate (22 gm., 0.186 mole) were condensed in the presence of sodium methylate catalyst (0.10 gm.) by the method of Homeyer (5). After removal of the excess ethyl carbonate *in vacuo* under nitrogen, an oil was obtained, yield 19.09 gm. (88.5%). This oil crystallized (m.p. 40–43°C.) on standing and two crystallizations from ethanol raised the melting point to 51.5–53°C. Calc. for $C_8H_{16}N_2O_2$: C, 55.80; H, 9.37; N, 16.27%. Found: C, 56.10; H, 9.41; N, 15.9%.

A sample (1.0 gm., 0.0058 mole) of 5-diethylaminomethyl-2-oxazolidone was refluxed with methyl iodide (0.825 gm., 0.0058 mole) in absolute methanol for 30 min. This solution was cooled to room temperature and allowed to stand for 15 hr. Colorless crystals (m.p. 158–161°C.) were deposited from the solution, yield 1.235 gm. (67.7%). Two crystallizations from absolute ethanol raised the melting point to a constant value of 160.5–161.5°C. Calc. for $C_9H_{19}IN_2O_2$: C, 34.41; H, 6.09; I, 40.39; N, 8.92%. Found: C, 34.22; H, 5.94; I, 40.58; N, 9.04%.

Infrared Spectra

The infrared spectra were obtained with a Perkin-Elmer single beam spectrophotometer equipped with a sodium chloride prism. The samples were observed as mulls of the solid in Nujol.

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FRACTIONATION OF POLYSACCHARIDES[1]

By A. J. Erskine[2,3] and J. K. N. Jones[3]

ABSTRACT

A method for fractionation of water-soluble polysaccharide mixtures has been examined, and by its use three of the four materials studied have been separated into two or more polysaccharide components. No fractionation of the fourth material could be detected.

In the study of polysaccharides one of the first requirements is that the material be chemically homogeneous, i.e. that further fractionation of the polysaccharide yields products having the same specific rotations and the same ratio of monosaccharide building units. Most reports of such work include attempts to fractionate the material in question. However, little effort has been made to develop standard methods for this purpose such as are used in protein chemistry. The method to be described has proved reasonably satisfactory for three of the four water-soluble polysaccharides investigated. It is hoped that the procedure may prove to be generally applicable, and later experiments may show whether it can be used to fractionate water-insoluble, alkali-soluble polysaccharide mixtures.

Methods of fractionation of polymers now in use are based upon many properties. Electrophoresis is one way of testing the chemical homogeneity of polysaccharide materials, but it can only be used to separate micro-quantities, and the same is true of the ultracentrifuge. These methods are not at present of preparative value, although they may give information which can be used to interpret or correct results obtained by other means. Solvent partition has been widely used for separating mixtures of methylated or acetylated polysaccharides, but the unsubstituted materials are usually too insoluble in solvents other than water to permit use of these methods. Consequently, most attempts to fractionate polysaccharides make use of precipitation and inevitably suffer from the faults of coprecipitation, occlusion, etc., as most precipitates so obtained are voluminous and jelly-like. In these respects the present method offers little or no improvement, but the ease with which the neutral components of polysaccharide mixtures are isolated is a definite advance.

In most cases a solution of precipitant is added to an aqueous solution of the polysaccharide. Occasionally alcohol will effect a partial separation of the components of a mixture (e.g., 5).[4] Recently Jones (12) found that cetyl trimethylammonium bromide could be used to precipitate the acidic components from a mixture of polysaccharides. Bailey (3) used solutions of baryta or sodium hydroxide with moderate success. However, the majority of workers have employed solutions of copper salts to effect separation of polysaccharides.

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[4]*The references cited are not the only cases in which a specific precipitant was used.*

Fehling's solution is often used (6), possibly because it is a common reagent in the laboratory, while solutions of "cupri-ethylenediamine" (4), cupric chloride (1), cupric sulphate (9), and cupric acetate (7) have also been used. In most cases an excess of precipitant is added and the precipitate is removed by either filtration or centrifugation. The "copper complex" is then decomposed by an alcoholic solution of acid or a chelating agent, and the precipitate washed until free from inorganic ions. Frequently a further precipitate is obtained from the filtrate by addition of alcohol, and this sequence of operations is sometimes repeated as many as thirty times.

This paper describes attempts to fractionate mixtures of polysaccharides using cupric acetate solution and ethanol as precipitants, but with the important difference that no more of each is added at any one time than is necessary to initiate precipitation. In this manner it was shown that the mucilage from linseed (*Linum usitatissimum*) is a mixture of not less than three distinct polysaccharides. This success led to attempts to fractionate other common plant mucilages. No fractionation of the mucilage from the bark of slippery elm (*Ulmus fulva*) could be detected, but the seed mucilages from *Plantago ovata* and *P. arenaria*[5] were each shown to contain at least two polysaccharide components. The constants determined to assess whether a fractionation had been effected were (1) optical rotation, (2) equivalent weight, and (3) paper chromatographic examination of the sugars produced upon hydrolysis of the fractions. In each case it was found possible to obtain one fraction containing less than one per cent of uronic acid after refractionation (see experimental section). Although similar in composition these fractions differ in optical rotation and evidently vary with their source.

These results may be compared with those obtained by earlier workers. It has been reported (3) that linseed mucilage can be fractionated by means of baryta, and Easterby and Jones (7) determined the proportions of sugars present in two fractions which were obtained from this material, using cupric acetate and ethanol as precipitants. It is evident from the constants reported for their fractions that these workers effected only a partial separation of linseed mucilage into its components. The failure to fractionate slippery elm mucilage is in agreement with the results of Gill *et al.*, who found it to be homogeneous when methylated (8). Laidlaw and Percival (13) studied *Plantago ovata* mucilage and observed that varying conditions of preparation yielded products with different properties. This was in agreement with the work of Anderson and Fireman (2) on the seed mucilage of *Plantago psyllium* (believed to be synonymous with *P. ovata*). Laidlaw and Percival (13) obtained two products, with equivalent weights of 700 and 4000 respectively, but upon methylation both gave uronic acid free polysaccharides of similar but not identical composition. The present work confirms that a neutral polysaccharide is present in *P. ovata* mucilage, and does not preclude the isolation of a polyuronide from the acidic component by further fractionation. Several groups of workers have investigated *Plantago arenaria* mucilage without

[5]*More correctly known by the older name P. indica (private communication by D. S. Erskine).*

attempting its fractionation (10, 11, 14), and here also a neutral polysaccharide was obtained upon methylation of a uronic acid containing material (14). Our results confirm the presence of a neutral compound and, as in the case of *P. ovata*, admit the possibility of isolating a polyuronide from the acidic component by refractionation.

EXPERIMENTAL

General Procedure

As far as was possible all materials were prepared under the same conditions. The raw materials—seeds or finely shredded bark—were stirred with 10 times their weight of water for six hours at room temperature. The mucilaginous solution was separated by pouring it through a Buchner funnel (without paper), followed by straining it through muslin. The polysaccharide was precipitated by pouring the solution into two volumes of absolute ethanol containing concentrated hydrochloric acid (10 ml./liter of ethanol) and enough ice to keep the reaction mixture at or below room temperature. The precipitated material was lifted out, washed with absolute ethanol to remove acid, and redissolved in about 15–20 times its weight of water. The aqueous solution was centrifuged to remove insoluble material, and cupric acetate solution (7%, w/v in water) was added until precipitation occurred. The precipitate was removed by centrifugation, and cupric acetate solution was added until a maximum concentration of 0.40% of cupric acetate was reached. If no precipitate had formed, ethanol was added portionwise and each precipitate so formed was removed before further precipitant was added. In all cases the copper complex was decomposed by twice macerating the precipitate in a Waring Blendor with absolute ethanol containing 5% v/v of concentrated hydrochloric acid for one minute or less. The resulting polysaccharides were washed with absolute ethanol until the washings gave a negative test for chloride, and were dried under vacuum to constant weight before examination.

For analysis a 50 mgm. (approx.) sample was weighed out and dissolved in water (5 ml.). The optical rotation of this solution was determined, if possible, and duplicate 1 ml. samples were titrated with $N/10$ sodium hydroxide solution, using an Agla micrometer syringe. A sample of the solution was hydrolyzed with N sulphuric acid at 90–95° for 24 hr., the acid was neutralized ($BaCO_3$ or $Ba(OH)_2$), and the resulting precipitate removed. The solution was concentrated and the sirup examined on paper chromatograms in the two solvent mixtures—ethyl acetate/acetic acid/formic acid/water, 18/3/1/4, and butanol/pyridine/water, 10/3/3. Sugars were identified by their rates of movement relative to a standard mixture of sugars.

The linseeds were obtained from W. Peters and Sons Seed Co., Kingston, Ont., while the slippery elm bark is a product of S. B. Penick & Co., Botanical Drugs, New York, N.Y. The *Plantago ovata* and *P. arenaria* seeds were samples of "Psyllium seed blond" and "Psyllium seed black" respectively, obtained from S. B. Penick & Co., and identified by D. S. Erskine, Department of Geography, University of Toronto, Toronto, Ont.

Linseed Mucilage

The polysaccharide mixture was prepared exactly as described above, in 4% yield. Samples prepared from seeds obtained at different times showed the same properties. The results from a typical fractionation are given in Table I. Fractions with similar properties were combined and refractionated,

TABLE I

FRACTIONATION OF LINSEED MUCILAGE

Fraction	% $CuAc_2$ for pptn.	% EtOH for pptn.	Fraction of starting material	$[\alpha]_D$	$c(H_2O)$	Equiv. wt.
I	0.18	0	21.0	+57°±10°	0.75*	—
II	0.41	16	53.2	+ 7°± 3°	1.11	646
III	0.25	49	9.0	−38°± 3°	1.08	2560
IV	0.18	64	10.8	−50°± 3°	1.04	24900

**In 0.03 N NaOH solution.*

giving, eventually, fractions with the properties shown in Table II. Further fractionation is being carried out on fractions *A* and *B* (Table II) in the hope

TABLE II

PROPERTIES OF POLYSACCHARIDES ISOLATED FROM LINSEED MUCILAGE

Fraction	% of total	$[\alpha]_D$	Equiv. wt.	Products on hydrolysis						
				Rham.	Fuc.	Xyl.	Ara.	Glu.	Gal.	G.A.
A	15	+95°±5°	390±20	+++	+	+++	+		+	+++
B	65	+10°±5°	550±30	+	+	Trace			+++	++
C	20	−49°±2°	—			+++	++	+	+	

Rham. = Rhamnose, Fuc. = Fucose, Xyl. = Xylose, Ara. = Arabinose, Glu. = Glucose, Gal. = Galactose, G.A. = Galacturonic acid.

of obtaining a pentose-free polysaccharide from the latter. No further separation of fraction *C* could be obtained and structural studies on this material are in progress.

Slippery Elm Mucilage

The slippery elm bark was shredded into fragments not larger than approx. 1/4 in. by 1/4 in. by 1/32 in., and extracted with benzene–ethanol solution (2/1, v/v) to remove oils and resinous materials. The preparation then followed the general procedure outlined above, and the polysaccharide was obtained as a crumbly light-brown solid in 8% yield. This material was very sparingly soluble in cold water, and almost completely insoluble in dilute alkali solutions, so fractionation was rather unsatisfactory. It was not possible to determine optical rotations of the fractions, and titration of their heterogeneous dispersions was accompanied by a high degree of error. Equivalent weights for the three fractions obtained in one operation varied from 520 to 580 which was

within the experimental error under those conditions. All fractions gave the same products upon hydrolysis, namely: rhamnose, 3-*O*-methyl galactose, galactose, and galacturonic acid, in approximately equal proportions, with a smaller amount of xylose.

Plantago ovata Mucilage

The seeds of *Plantago ovata* gave an exceedingly viscous solution with water. Even when dispersed in 25 times their weight of water the suspension could not be filtered upon a Buchner funnel in the usual manner, but when it was left overnight the seeds and a dense gel settled out and the clear solution on top could be decanted. Similarly, centrifugation gave a clear solution and a gel, which were fractionated separately. Upon refractionation the components listed in Table III were obtained.

TABLE III

PROPERTIES OF FRACTIONS OBTAINED FROM *Plantago ovata* MUCILAGE

Fraction	% of total	$[\alpha]_D$	$c(H_2O)$	Equiv. wt.	Products on hydrolysis					
					Rham.	4mGl.A.	Xyl.	Ara.	Gal.	G.A.
(*S*)olution 1	9	+ 23°	1.14	710	++	Trace	+++	++	+	++
*S*2	12	− 40°	1.16	1300	+	Trace	+++	+	+	+
*S*3	15	−108°	0.92	34000			+++	+	Trace	
(*G*)el 1	54	—	—	2400	+	+	+++	++	+	+
*G*2	10	− 68°	0.58	1900						

Rham., Xyl., Ara., Gal., G.A., as in Table II; 4mGl.A. = 4-O-methyl glucuronic acid.

From these properties it is thought likely that refractionation of *S*2 and *G*2 would yield largely the product present in *S*3, which is qualitatively similar to that isolated after methylation by Laidlaw *et al.* (13). Fraction *S*1 is presumably the same as their polysaccharide *P*1, to which it corresponds closely in equivalent weight and composition. Their work suggests that refractionation of our product might separate a component, containing all of the rhamnose and galacturonic acid, with a still lower equivalent weight. Fraction *G*1 contains some impurity that renders it relatively insoluble in water, but the concentration of an acidic sugar assumed from its rate to be 4-*O*-methyl glucuronic acid (not previously detected in this material) in this fraction suggests that yet a third polysaccharide may be involved.

Plantago arenaria Mucilage

The polysaccharide mixture was prepared and fractionated as described in the general procedure. As before, the fractions initially precipitated gave more opaque solutions than those isolated later, but most unexpectedly it was found that the acidic fraction was the last to be precipitated. A relatively small amount of an acidic polysaccharide was obtained from the last fraction, and this is in agreement with earlier results (10, 11, 14). As in the case of *Plantago ovata* previous workers found no uronic acid or rhamnose in their methylated products, so here again the isolation of a polyuronide upon refractionation may be possible.

TABLE IV

PROPERTIES OF FRACTIONS OBTAINED FROM *Plantago arenaria* MUCILAGE

Fraction	$[\alpha]_D$	Equiv. wt.	Products on hydrolysis				
			Rham.	Xyl.	Ara.	Gal.	G.A.
A 1*a*	—	25000		+++	++	+	
A 1*b*	—	12000		+++	++	+	
A 1*c*	−54°	19000		++	+	+	
A 2	−42°	3500					
B 1*a*	−55°	25000		++	++	+	
B 1*b*	—	7100		+++	++	+	
B 2	+45°	670	++	++	++	+	++

Abbreviations as before.

ACKNOWLEDGMENT

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PREPARATION OF GUANIDINE FROM UREA, SULPHUR DIOXIDE, AND AMMONIA UNDER PRESSURE[1]

By Jean L. Boivin

ABSTRACT

It has been found that guanidine can be prepared in good yield from urea, sulphur dioxide, and ammonia under pressure over a wide range of conditions. A study of the effect of concentration, temperature, time, and pressure has been made. A part of the sulphur dioxide introduced into the reaction vessel can be recovered as elemental sulphur. Guanidine nitrate is easily prepared by treating the reaction product with dilute nitric acid. The mechanism of this synthesis has been found to proceed through the formation of ammonium sulphamate from sulphur dioxide and ammonia. Guanidine was present as the sulphamate when synthesized at low temperatures and as the sulphate at high temperatures.

Ammonia and sulphur trioxide react under suitable conditions to yield ammonium sulphamate (Eq. 1) with some triammonium imidosulphonate (Eq. 2) and sulphamide (Eq. 3).

$$SO_3 + 2NH_3 \rightarrow H_2NSO_3NH_4 \quad [1]$$

$$2SO_3 + 3NH_3 \rightarrow NH_4N(SO_3NH_4)_2 \quad [2]$$

$$SO_3 + 2NH_3 \rightarrow NH_2SO_2NH_2 + H_2O \quad [3]$$

The complex product, obtained from ammonia and sulphur trioxide, is known to yield guanidine sulphamate when heated under pressure with urea and ammonia (3). For convenience of description, only the ammonium sulphamate will be considered, since analogous reactions can be inferred for the other two compounds.

The reaction of sulphur dioxide and ammonia, although not clearly understood, is believed to be similar to that with sulphur trioxide and ammonia.

$$SO_2 + 2NH_3 \rightarrow H_2NSO_2NH_4 \quad [4]$$

$$2SO_2 + 3NH_3 \rightarrow H_4N{-}N(SO_2NH_4)_2 \quad [5]$$

$$SO_2 + 2NH_3 \rightarrow H_2NSONH_2 + H_2O \quad [6]$$

In the actual preparation of this complex, an excess of ammonia is reacted with sulphur dioxide. The reaction is exothermic. A nearly white product is obtained, but there is always present a red substance which is reported to be triammonium imidosulphinate (1).

When urea, sulphur dioxide, and ammonia are reacted in the molar ratio of 1:3:7 under suitable conditions, urea is converted into guanidine in yields exceeding 80%. It has been found, however, that in all cases one third of the sulphur dioxide taken is recovered in the form of elemental sulphur, which is easily filtered. The filtrate, after evaporation to small volume and treatment with excess of dilute nitric acid, yields guanidine nitrate while some sulphur dioxide is evolved.

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In view of the presence of sulphur in the reaction mixture, it appears that an oxidoreduction process takes place, possibly according to the over-all equation

$$2H_2N{-}\overset{\uparrow}{\underset{O}{S}}{-}ONH_4 + \overset{\uparrow}{\underset{O}{S}}{=}O \rightarrow S + 2(NH_4)_2SO_4. \qquad [7]$$

However, an alternative mechanism could be considered for the formation of sulphur. The amount of sulphur found in the present synthesis of guanidine was nearly constant at one mole when three moles of sulphur dioxide was used; this equation accounts for formation of sulphur and sulphate.

A preliminary investigation of the factors involved in this synthesis of guanidine from urea has been made. In all cases, the ammonia – sulphur dioxide complex was formed below −30° C. in the glass liner of an ordinary Parr bomb, and urea was added to the mixture. After the mixture was heated to the desired temperature over a period of time under ammonia pressure, the mass, which was still liquid at 150° C., was boiled in water. Sulphur was removed by filtration and the filtrate was analyzed for guanidine and melamine contents.

TABLE I

EFFECT OF TEMPERATURE

Urea: 0.1 mole; sulphur dioxide: 0.3 mole; ammonia: 0.7 mole; pressure: 200 p.s.i.g.; heating time: 1 hr.

Temp., °C.	Yield based on urea guanidine, %	Melamine, %
215	1	0
235	64	0
245	80	0
265	81	0
275	76	6.1
285	51	17
295	46	35
305	42	44

Effect of Temperature

It can be seen that 80% yield of guanidine (Table I) can be obtained between 245° C. and 265° C. under the present conditions without the production of melamine which is due to the decomposition of the guanidine formed. The guanidine formation increased with temperature, reached a maximum value, and then decreased when melamine appeared in the mixture.

TABLE II

EFFECT OF CONCENTRATION OF UREA

Sulphur dioxide: 0.3 mole; ammonia: 0.7 mole; temp.: 275°C.; pressure: 200 p.s.i.g.; heating time: 1 hr.

Urea, mole	Yield based on urea guanidine, %	Melamine, %
0.05	60	0
0.10	74	0
0.15	56	0
0.20	43	10.3
0.30	26	8.1

Effect of Concentration of Urea

The optimum amount of urea seemed to be one tenth of a mole under the actual conditions (Table II). At high concentrations of urea, a considerable amount of cyanuric acid was found in addition to unreacted urea.

Effect of Time

The effect of the period of heating has been studied at 255°, 275°, and 305° C. The reaction time given is measured from the attainment of the stated temperature.

TABLE III

EFFECT OF TIME

Urea: 0.1 mole; sulphur dioxide: 0.3 mole; pressure: 200 p.s.i.g.; ammonia: 0.7 mole

Temp., °C.	Time, min.	Yield based on urea guanidine, %
255	30	73
255	60	81
255	90	72
275	30	82
275	60	74
275	90	70
305	5	51
305	10	57
305	15	55
305	60	42

It can be noted that a higher temperature decreases the heating time (Table III). The reaction seems to proceed twice as fast when temperature is increased by 20° C. However, at 305° C. optimum yield is low and it seems that this reaction could not be effected with good yields at high temperature with the equipment used.

Effect of Pressure

From the point of view of equipment design and operation, pressure requirements frequently have a major influence on cost and safety. In the reaction, the effect of pressure is negligible from 200 to 3000 p.s.i.g., as can be seen in Table IV. Even under a pressure of 75 p.s.i.g., a 74% yield could be obtained.

TABLE IV

EFFECT OF PRESSURE

Urea: 0.1 mole; sulphur dioxide: 0.3 mole; temp.: 275°C.; heating time: 30 min.

NH_3, mole	Pressure, p.s.i.g.	Guanidine, %
2.0	3000*	83
2.0	1000*	82
0.7	200*	82
0.7	75*	74
0.7	0	46

**Vented to this pressure, after attaining prescribed temperature.*

Good yields may be obtained over a wide range of conditions. Pressures as low as 75 p.s.i.g. are capable of giving 75% yield. This would simplify the construction of a reaction vessel. An important feature is ready isolation of guanidine in the form of its nitrate. In view of the good yields obtained and the cheap starting materials used, special attention was devoted to elucidate the mechanism of the synthesis.

A review of the literature dealing with ammonium amidosulphinate was not too conclusive for the elucidation of the mechanism. Divers and Ogawa (1) found that ammonium amidosulphinate when heated yields ammonia and ammonium imidosulphinate, a reaction similar to the formation of ammonium imidosulphonate from ammonium sulphamate. They also explain that the reaction between ammonia and sulphur dioxide yields mainly ammonium imidosulphinate, the latter decomposing on heating into volatile matter, sulphur, ammonium sulphate, and ammonium imidosulphinate. In spite of the numerous products isolated from the decomposition of the ammonia – sulphur dioxide complexes, the reaction under ammonia pressure is less intricate because of the recovery of sulphur which has always been made in 33% yield based on sulphur dioxide used. Guanidine was produced in high yields from urea under various conditions of temperature and pressure.

In the following discussion of the explanation of this reaction mechanism, experiments have been made as quantitative as possible considering the difficulties encountered when working with gaseous products and heating them in a bomb at high temperatures.

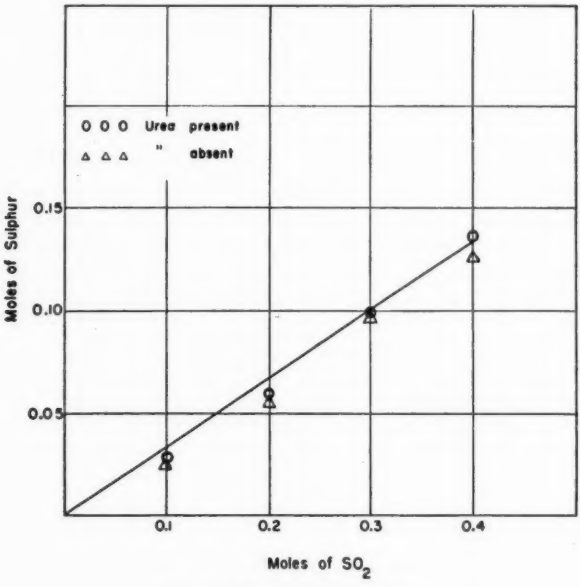

FIG. 1. Formation of sulphur.

Sulphur Formation

By heating together a mixture of urea, sulphur dioxide, and ammonia at 275° C. for half an hour, the yield of guanidine from urea was nearly constant at 80%, when the molar ratio of urea: sulphur dioxide: ammonia was 1:3:9. The variation of the amount of sulphur dioxide used resulted in a variation in the yield of guanidine from urea (Table V). It should also be noted that the formation of sulphur increased with the amount of sulphur dioxide added to the reaction mixture, the yield being nearly constant at 33%. If a graph is made by plotting the molar amounts of sulphur produced against the molar quantities of sulphur dioxide used, a straight line is obtained (Fig. 1).

To prove that urea had no participation in the reaction involving the production of sulphur, the same series of experiments were effected in its absence (Table VI). It was found that sulphur was produced in nearly the same yield as when urea was present.

It was also thought that the formation of sulphur might be an equilibrium reaction. An experiment was made (No. 84, Table V) in which sulphur was added to the reaction mixture. The total amount of sulphur was nearly equal to the sulphur added and the sulphur usually produced from sulphur dioxide.

TABLE V

SULPHUR BALANCE IN THE FUSION OF UREA, SULPHUR DIOXIDE, AND AMMONIA

Run No.	SO_2, mole	Urea, mole	NH_3, mole	Sulphur produced, mole	$BaSO_4$(O), mole *A*	$BaSO_4$(HCl) mole *B*	*A* − *B*	Guanidine, mole	Pressure, p.s.i.g.	Sulphur balance, mole
83	0.1	0.1	0.9	0.0293	0.080	0.058	0.022	0.042	2400	0.109
82	0.2	0.1	0.9	0.061	0.142	0.076	0.066	0.069	1850	0.203
81	0.3	0.1	0.9	0.098	0.212	0.128	0.084	0.083	1400	0.310
85	0.4	0.1	0.9	0.132	0.260	0.118	0.142	0.073	800	0.392
84	0.3–0.1255*	0.1	0.9	0.196	0.209	0.133	0.076	0.076	200 (vented)	0.405

**Elemental sulphur added.*

NOTE: *The bomb was heated at 275°C. for 30 min. in all the above experiments.*

Thus the addition of sulphur does not appreciably depress its formation; therefore, in the actual synthesis the formation of sulphur does not result from an equilibrium reaction.

Sulphate Formation

Since sulphates were present in the reaction mixture, experiments were carried out to determine the effect of urea on the ammonia – sulphur dioxide complex. After the ingredients had been heated in the same way as mentioned in Tables I and II, the reaction products were dissolved in water and the solution filtered free of sulphur. The filtrate was analyzed for sulphate ion content. It was to be expected that the reaction mixture might contain reducing sulphur compounds like sulphites and thiosulphates, and that a determination of the actual sulphate would be of value. The method involved the cold treatment of a portion of this solution with barium chloride in hydrochloric acid. Results are given in Tables V and VI and shown graphically in Figs. 2 and 3. It can be seen that the molar quantities of sulphate produced from sulphur dioxide are nearly linear in the absence of urea.

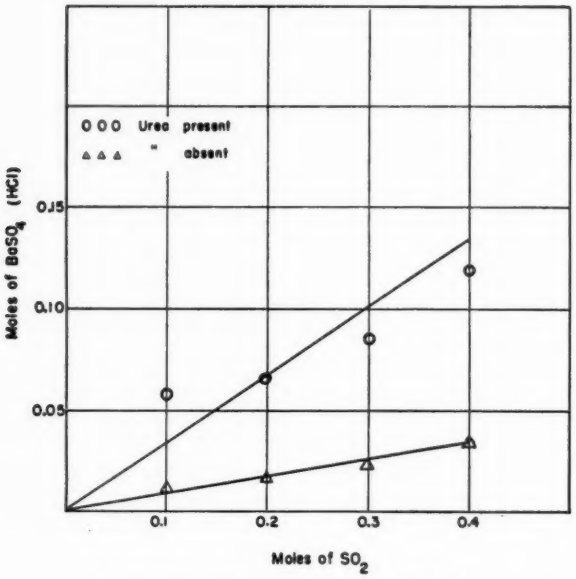

FIG. 2. Formation of barium sulphate (HCl).

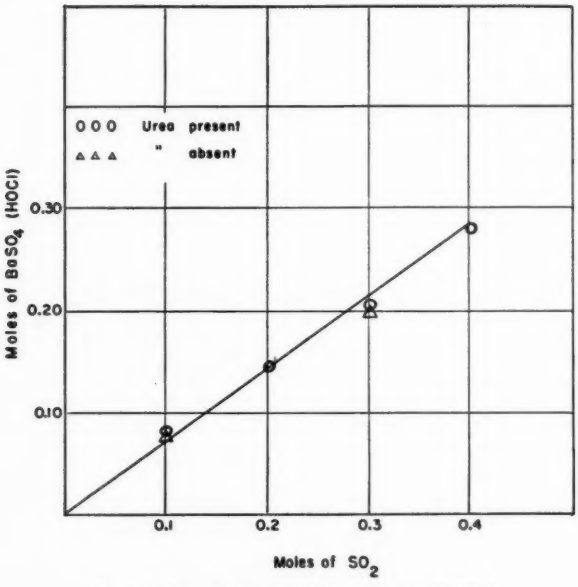

FIG. 3. Formation of barium sulphate (HOCl).

However, what is important in these experiments is the marked increase of sulphate formed when urea is present, i.e. when guanidine is produced.

TABLE VI

SULPHUR BALANCE IN THE REACTION OF SULPHUR DIOXIDE AND AMMONIA

Batch No.	SO_2, mole	NH_3, mole	Pressure, p.s.i.g.	NH_3 recovered in moles	NH_3 used	Sulphur produced in moles	$BaSO_4(O)$, mole *A*	$BaSO_4(HCl)$, mole *B*	*A* − *B*	Sulphur balance, mole
86	0.1	0.9	2800	0.62	0.28	0.025	0.072	0.013	0.059	0.097
87	0.2	0.9	2200	0.55	0.35	0.057	0.143	0.019	0.124	0.201
88	0.3	0.9	1700	0.35	0.55	0.102	0.200	0.024	0.176	0.302
89	0.4	0.9	950	0.25	0.65	0.123	0.278	0.037	0.241	0.401

NOTE: *The bomb was heated at 275°C. for 30 min.*

The determination of total sulphur-containing compounds in the form of sulphate was thought to be of interest in view of obtaining a good sulphur balance. The estimation was made by oxidizing the reducing sulphur compounds present in the solution to sulphate by means of sodium hypochlorite. Fig. 3 shows that the sulphate content, expressed in moles of barium sulphate, increases linearly with increasing amounts of sulphur dioxide, with or without urea, the molar values of sulphate being the same.

Ammonium Sulphamate

If subtraction is made between the molar value of sulphate present after the oxidation of the solution ($BaSO_4(O)$) and the molar quantity of true sulphate ($BaSO_4(HCl)$) when urea was present, values are obtained which are nearly proportional to the quantities of sulphur dioxide present up to 3 moles per mole of urea (Fig. 4).

$$BaSO_4(O) - BaSO_4(HCl) = C$$

This value "*C*" was found to be equal to the molar quantities of guanidine produced from urea. For instance, in Table V, run No. 81 shows the molar quantity of sulphates formed. This value "*C*" is: 0.212−0.128 = 0.084. Hence this value "*C*" is related to the formation of guanidine.

Results also show that the amount of oxidized sulphur-containing compounds as barium sulphate (Tables V and VI), either in the presence of urea or in its absence, is proportional to the amount of sulphur dioxide present in the reaction mixture (Fig. 3).

Moreover, if summation of molar quantities of elemental sulphur and total sulphates formed is made, a good sulphur balance is obtained, as for instance in run No. 82 of Table V and in run No. 87 of Table VI.

From the data of Tables V and VI, proportionality of production of sulphur has been observed in respect to sulphur dioxide in the presence or absence of urea; the same fact has been observed of the actual sulphate present when urea was added to the ammonia – sulphur dioxide complex. In its absence, this value "*C*" was proportional to the amount of sulphur dioxide used (Fig. 4).

Therefore, there is a relationship between the formation of sulphates, sulphur, and guanidine. It was thought that the ammonium sulphamate

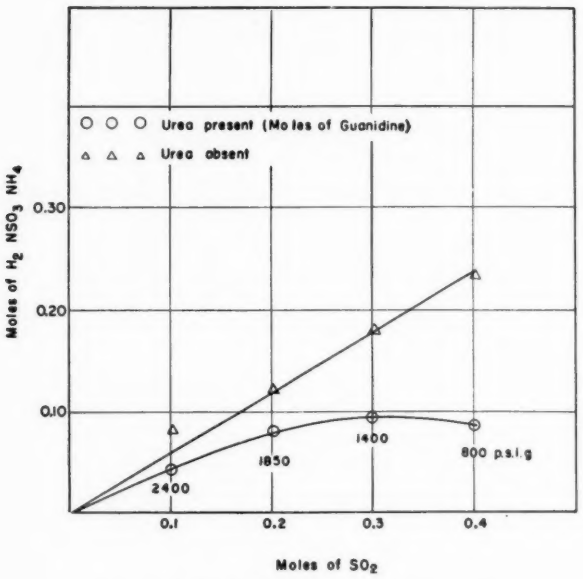

FIG. 4. Formation of ammonium sulphamate.

isolated in low yields by Divers and Ogawa (1) when they heated the ammonia – sulphur dioxide complex was probably the predominant compound under the actual conditions where excess of ammonia is used. If so, guanidine should be present as the sulphamate or sulphate. Guanidine sulphamate is soluble in liquid ammonia and slightly soluble in ethanol whereas guanidine sulphate is insoluble in both solvents. By extraction of the reaction products with liquid ammonia, guanidine sulphamate was identified and isolated in good yields.

After the isolation of guanidine sulphamate, there was evidence that the actual synthesis was a sulphamate synthesis of guanidine from urea. Therefore, the heating of sulphur dioxide with excess of ammonia under pressure should yield ammonium sulphamate and sulphur as the main products, ammonium sulphate being present in quantities equivalent to the guanidine formed.

When sulphur dioxide and ammonia were heated at 275° C. for half an hour (Table VI), the reaction mixture contained molten products at 125° C. The melt was extracted with liquid ammonia and the solution filtered. After evaporation, a crystalline product was obtained which was found to be ammonium sulphamate. The yields of ammonium sulphamate were excellent.

Mechanism of the Synthesis

The mechanism of the formation of ammonium sulphamate can be thus explained. At low temperature an ammonia – sulphur dioxide complex will be

formed consisting of ammonium amidosulphinate (Eq. 8) and ammonium imidosulphinate (Eq. 9).

$$SO_2 + 2NH_3 \underset{100\text{–}150°C.}{\overset{-10°C.}{\rightleftharpoons}} H_2N—SO_2NH_4 \quad [8]$$

$$2SO_2 + 3NH_3 \underset{100\text{–}150°C.}{\overset{-10°C.}{\rightleftharpoons}} NH\begin{matrix}SO_2NH_4\\SO_2NH_4\end{matrix} \quad [9]$$

But by heating these two compounds in excess of ammonia, they should dissociate incompletely yielding ammonia and sulphur dioxide.

It is known that sulphur dioxide activated by light (2) dissociates into colloidal sulphur and sulphur trioxide according to the following equilibrium reaction:

$$3SO_2 \rightleftharpoons S + 2SO_3. \quad [10]$$

If so, the formation of ammonium sulphamate will be readily explained from sulphur dioxide and ammonia:

$$SO_3 + 2NH_3 \longrightarrow H_2NSO_3NH_4. \quad [11]$$

In this synthesis the formation of sulphur has been found to take place at about 150° C. It may be deduced that, owing to thermal activation of the sulphur dioxide molecule, it should dissociate in the presence of ammonia, as above, yielding sulphur and sulphur trioxide. Thus the over-all reaction of sulphur dioxide and ammonia will be represented by the following equation:

$$3SO_2 + 4NH_3 \longrightarrow S + 2NH_2SO_3NH_4. \quad [12]$$

The isolation of guanidine sulphamate from a mixture of urea, sulphur dioxide, and ammonia in molar ratio 1:3:9 is not surprising. From experiments described earlier it has been found that guanidine is produced at a temperature

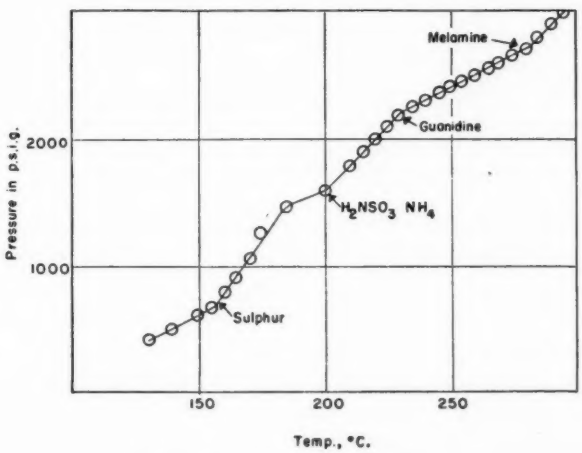

FIG. 5. Pressure–temperature curve.

of about 220° C. Sulphur is formed at a temperature as low as 160° C., therefore sulphamate should be produced. This is shown graphically in Fig. 5 where pressure is plotted against the temperature.

The synthesis of guanidine from urea, sulphur dioxide, and ammonia under pressure proceeds in two main steps. First ammonium sulphamate is produced from sulphur dioxide and ammonia:

$$3SO_2 + 4NH_3 \longrightarrow 2NH_2SO_3NH_4 + S \qquad [13]$$

then urea reacts with ammonium sulphamate yielding guanidine sulphamate:

$$\begin{matrix} NH_2 \\ | \\ C{=}O \\ | \\ NH_2 \end{matrix} + 2NH_2SO_3NH_4 \longrightarrow \begin{matrix} NH_2 \\ | \\ C{=}NH \\ | \\ NH_2.NH_2SO_3H \end{matrix} + (NH_4)_2SO_4 \qquad [14]$$

$$3SO_2 + 4NH_3 + \begin{matrix} NH_2 \\ | \\ C{=}O \\ | \\ NH_2 \end{matrix} \longrightarrow \begin{matrix} NH_2 \\ | \\ C{=}NH \\ | \\ NH_2.NH_2SO_3H \end{matrix} + (NH_4)_2SO_4 + S \qquad [15]$$

Guanidine Sulphamate and Sulphate

The formation of guanidine increased, as was expected, with the amount of sulphur dioxide used (Fig. 4), but decreased owing to dilution with excess of sulphur dioxide (0.4 mole vs. 0.1 mole urea). When a mixture of urea, sulphur dioxide, and ammonia (molar ratio 1:3:9) was heated at 275° C. for an hour at a pressure of 200 p.s.i.g., guanidine was present mainly as the sulphamate. Alternatively, the same reaction mixture heated at 300° C. for two to five minutes and cooled immediately yielded mainly guanidine sulphate. Guanidine sulphamate is soluble in liquid ammonia whereas guanidine sulphate is very insoluble. Therefore a means of separating the two salts of guanidine is suggested.

When urea, sulphur dioxide, and ammonia were used in the molar ratio 2:3:7, guanidine sulphate was produced in 43.6% yield, traces of guanidine sulphamate being formed. Melamine was obtained also in good yield owing to the instability of guanidine sulphate under the conditions employed. At a lower temperature of synthesis, for instance at 275° C., less melamine is produced, but the yield of guanidine sulphate is decreased. The reactions involved when two moles of urea are used are as follows:

$$2\begin{matrix} NH_2 \\ | \\ C{=}O \\ | \\ NH_2 \end{matrix} + 3SO_2 + 4NH_3 \longrightarrow \left(\begin{matrix} NH_2 \\ | \\ C{=}NH \\ | \\ NH_2 \end{matrix} \right)_2 .H_2SO_4 + S + (NH_4)_2SO_4$$

Guanidine Nitrate

A series of runs were made at 275° C. from urea, sulphur dioxide, and ammonia (molar ratio 1:3:7) under which conditions 80% yield of guanidine or better was obtained. The reaction products were dissolved in boiling water, sulphur was filtered, and the filtrate treated with various quantities of nitric acid. Table VII shows the proportions and the amounts of guanidine nitrate

TABLE VII

GUANIDINE NITRATE

Run[1] No.	HNO_3 (70%), gm.	Molar ratio, urea: HNO_3	Crude G.N.[2]		Recrystallized G.N.[3] from 20 ml. of water		% Yield of G.N. from urea
			gm.	m.p., °C.	gm.	m.p., °C.	
1	9.0	1:1	9.5	190–195	8.4	204–206	69
2	10.8	1:1.2	10.0	192–196	8.9	205–207	73
3	12.6	1:1.4	10.0	190–195	8.8	204–206	72
4	14.4	1:1.6	8.6	196–199	7.6	204–206	62
5	16.2	1:1.8	8.2	195–198	7.2	205–207	59

[1]*All runs were prepared by heating at 275°C. for half an hour at 200 p.s.i.g., urea:SO_2:NH_3 molar ratio being 1:3:9.*
[2]*Crystallization at 0°C. from 50 ml. of solution. G.N. = guanidine nitrate.*
[3]*Recrystallization at 0°C. from 20 ml. of water.*

isolated. The yields are very good if correction is made for solubility. It should be noted that a maximum yield of guanidine nitrate is obtained when the guanidine – nitric acid ratio is 1: 1.35. Thus a yield of guanidine nitrate of 73% based on urea is obtained.

Conclusion

The synthesis of guanidine from urea, using sulphur dioxide and ammonia as dehydrating agent, is promising in that the starting materials are cheap and easily accessible. The ease of handling of sulphur dioxide and the large amount of this chemical distributed as sulphur or pyrites could render this synthesis applicable to continuous production of guanidine. This can be achieved by feeding an ammonia solution of urea and sulphur dioxide in a suitable reactor maintained at the desired temperature. The reaction products are molten at a temperature as low as 120° C.

EXPERIMENTAL

General Procedure

A 100 ml. autoclave was charged with urea, sulphur dioxide frozen in liquid air, and liquid ammonia. The bomb was heated at the desired temperature for a period of time. After the bomb was cooled, the contents of the glass liner was dissolved in water, sulphur was filtered off, and the clear solution used for analytical work.

Estimation of Sulphur

The crude sulphur obtained by filtration was dissolved in carbon disulphide and the solution evaporated in a weighed dish. Sulphur is reported in moles (Tables V and VI).

Estimation of Sulphates

(*a*) A 10 ml. aliquot portion of the solution made up to 500 ml. was diluted with 200 ml. of water and treated at room temperature with 50 ml. of 10% $BaCl_2$ solution in 2% hydrochloric acid. $BaSO_4$(HCl) is reported in moles (Tables V and VI).

(*b*) A 10 ml. aliquot portion was diluted with 100 ml. of water; 10 ml. of sodium hypochlorite (5% available chlorine) was added and the solution

boiled. Hydrochloric acid was added until pH of 1–2 and then 50 ml. of 10% barium chloride added at the boiling point. The precipitate was filtered and weighed. $BaSO_4(O)$ is reported in moles (Tables V and VI).

Isolation of Guanidine Sulphamate

A mixture of urea (6.0 gm., 0.1 mole), sulphur dioxide (19.2 gm., 0.3 mole), and ammonia (15.3 gm., 0.9 mole) was heated at 275° C. for half an hour. The bomb was vented to 200 p.s.i.g. The contents of the glass liner was dissolved in water and sulphur was filtered off. The filtrate, after evaporation to dryness under reduced pressure, was treated with liquid ammonia (200 ml.) and the mixture filtered free of insoluble sulphates. The residue was washed well with ammonia. Analysis of the residue insoluble in liquid ammonia showed only traces of guanidine, presumably the sulphate. The liquid ammonia solution was allowed to evaporate and a residue was left which melted at 80–100° C. This material was recrystallized from alcohol and melted at 127° C. Further crystallizations raised the melting point to 128.5° C. A mixed melting point determination with guanidine sulphamate was not depressed.

Guanidine Sulphate

A similar batch was made by heating continuously to 300° C. and allowing the bomb to cool to 275° C. At this temperature the bomb was cooled with hot water and finally cold water. By working up the reaction products as above, it was found that the material insoluble in liquid ammonia contained 1.96 gm. of guanidine as sulphate and the liquid ammonia soluble material, 0.190 gm. of guanidine as sulphamate, thus giving a ratio of guanidine sulphamate to guanidine sulphate of 1:10.

When the amount of urea was doubled leaving the quantities of other ingredients the same as above, all the guanidine was present as sulphate. A 43.6% yield of guanidine based on urea was obtained. The other part of urea was transformed into melamine.

Guanidine Nitrate

A series of batches from urea, sulphur dioxide, and ammonia (molar ratio 1:3:9) was prepared by heating at 275° C. for half an hour. The reaction products were dissolved in water and the sulphur was removed by filtration. The filtrate was treated with a known amount of 70% nitric acid (Table IV) and the solution evaporated on the hot plate to a volume of 50 ml. The solution was cooled to 0° C. and allowed to stand at this temperature for 10 min. The solid was filtered and washed once with water at 0° C. The melting point of guanidine nitrate was taken. The guanidine nitrate obtained was usually contaminated with urea nitrate. A recrystallization from 20 ml. of water gave a guanidine nitrate melting above 200° C. In Table VII it is seen that the optimum ratio of HNO_3 to guanidine is 1.35 to 1.

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NOTES

PALLADIUM AND SUBSTITUTED QUINOLINES

By D. E. Ryan

The structures suggested for the compound precipitated from palladous chloride solutions by 6-nitroquinoline have been based on the composition $Pd(C_9H_6NNO_2)_2$ (1, 2). It was reported recently, however, that chloride was present in the precipitated complex; analysis showed that an addition compound, $Pd(C_9H_6NNO_2)_2Cl_2$, was the product of the reaction between 6-nitroquinoline and palladous chloride (3). In the study of substituted quinolines as organic precipitants qualitative tests on their reaction with palladous chloride solutions were carried out and the results are of interest.

Ten milliliter samples of palladous chloride solution, containing approximately 1 mgm. Pd per ml., were diluted to 100 ml. with distilled water and the samples (pH 3) placed on the steam bath. A small amount of the quinoline being investigated was added and the samples allowed to digest for half an hour. Yellow precipitates were obtained with the following 15 compounds:

quinoline	6-methoxyquinoline	2-chloroquinoline
6-nitroquinoline	6-phenylquinoline	4-methylquinoline
6-methylquinoline	8-nitroquinoline	8-nitro-4-methylquinoline
6-bromoquinoline	8-methylquinoline	8-chloro-4-methylquinoline
6-chloroquinoline	8-chloroquinoline	benzo(f)quinoline

1,2,3,4-Tetrahydroquinoline reduced palladium II to the metal.

The results confirm that the nitro group is unimportant in the reaction of 6-nitroquinoline with palladous chloride solutions. Substitution for the nitro group, and the position of substituents on the quinoline nucleus, do not affect markedly the ability of the compound to replace chloride in $PdCl_4''$ to precipitate $(quinoline)_2PdCl_2$; such complexes can be extracted by organic solvents. Similar reactions were observed on adding the compounds to $PtCl_4''$ solutions. The failure to obtain precipitates from palladous chloride solutions containing excess cyanide or thiocyanate suggests that the quinolines are unable to displace ions from strong complexes such as $Pd(CN)_4''$.

The results emphasize that substituted quinolines react to form molecular rather than ionic complexes with palladium II; on the other hand it is well known that platinum IV, as $PtCl_6''$, reacts with quinolines to precipitate temperature dependent ionic complexes, $(quinoline\ H)_2PtCl_6$.

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THE HEMICELLULOSE OF THE FOSSILIZED WOOD OF CEDRUS PENHALLOWII

By J. K. N. Jones and E. Merler

We were supplied with a sample of holocellulose from wood of a prehistoric tree, *Cedrus penhallowii*, through the kindness of Dr. J. R. W. Vallentyne of Queen's University and Dr. E. S. Barghoon of Harvard University. The residual holocellulose, prepared by extracting the extractive free wood with sodium chlorite followed by ammonia, was a white powder which contained relatively large amounts of silica.

The holocellulose was extracted with a cold potassium hydroxide – borate solution (20:4% w/v) in order to remove the hemicellulose fraction. The insoluble residue gave on hydrolysis glucose and traces of mannose. On addition of Fehling reagent to an aqueous solution of the extract, two fractions were obtained. The insoluble copper complex (70%) was decomposed with dilute acid and precipitated by the addition of alcohol. The resulting white powder gave on hydrolysis a mixture of sugars—glucose, mannose, xylose, and glucuronic acid. The fraction (5%) which did not form a copper complex was isolated after acidification with glacial acetic acid and precipitation by the addition of alcohol. On hydrolysis this fraction gave glucose. The sugars were detected chromatographically.

This wood, which grew in the Myocene era and which may be 10–20 million years old, contains a hemicellulose which seems not to differ greatly from that found in living softwoods. However, 4-*O*-methyl-D-glucuronic acid, which was not detected in the hydrolyzate from the prehistoric wood, is present in many softwoods of recent origin.

Methylation studies are in progress on these materials.

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4,6-*O*-*iso*PROPYLIDENE-METHYL-α-D-GLUCOSIDE

By J. K. N. Jones

When acetone condenses with sugars and sugar glycosides a five-membered ring ketal is usually formed (cf. 1,2-mono- and 1,2:5,6-di-*O*-*iso*propylidene-D-glucose, 2,3-*O*-*iso*propylidene-methyl-α-D-mannoside (1), and 3,4-*O*-*iso*propylidene-methyl-β-D-galactoside), but when a primary alcohol group is engaged in ring formation a six-membered ring may result. For example L-sorbose yields 2,3:4,6-di-*O*-*iso*propylidene-L-sorbose and D-xylose gives 1,2:3,5-di-*O*-*iso*propylidene-D-xylose, but D-mannose on condensation with acetone yields the 2,3:5,6-di-*O*-*iso*propylidene derivative.

Methyl-α-D-glucoside will also give a 4,6-*O*-*iso*propylidene derivative (two six-membered rings with a *trans* junction); cf. (1, p. 1019). This is not unexpected since the hydroxyl groups on C_4 and C_6 of both the mannoside and glucoside are similarly situated. Acetone thus behaves like aldehydes in that it can yield six-membered rings on condensation with sugar derivatives (3, 4, 5).

The structure of the *O-iso*propylidene derivative of methyl-α-D-glucoside was proved in the following manner. It gave a 2,3-di-*O*-tosyl, a 2,3-di-*O*-mesyl, a 2,3-di-*O*-benzoyl, and a 2,3-di-*O*-methyl derivative the structure of which was proved because it could be hydrolyzed to the known 2,3-di-*O*-methyl-α-D-glucoside. The original 4,6-*O-iso*propylidene derivative was hydrolyzed by dilute acetic acid, with the regeneration of methyl-α-D-glucoside, and was oxidized by sodium *meta*periodate thus proving that it possessed hydroxyl groups on adjacent carbon atoms.

EXPERIMENTAL

4,6-O-Isopropylidene-methyl-α-D-glucoside

Methyl-α-D-glucoside (10 gm.) was added to a solution of anhydrous zinc chloride (30 gm.) in acetone (200 ml.) and the mixture was boiled under reflux until a clear solution resulted (overnight). The cooled solution was poured onto a mixture of ice and a saturated solution of sodium carbonate. When all the ice had melted the solution was filtered and the alkaline filtrate concentrated under reduced pressure to *ca.* 250 ml. The cooled concentrate was then exhaustively extracted with chloroform. Concentration of the chloroform extract yielded 4,6-*O-iso*propylidene-methyl-α-D-glucoside (5.5 gm.) as a sirup which slowly crystallized. The crude product was crystallized with difficulty from benzene or from acetone – ether – light petroleum (b.p. 60–110°C.) mixture. It usually separated as a jelly which crystallized on standing. Sometimes crystalline material was obtained without the intermediate formation of jelly. The pure product (3.5 gm.) had m.p. 84–86°C., $[\alpha]_D$ +94°C. (c. 5.0, in water), and on hydrolysis with hot dilute acetic acid gave acetone, detected by its odor and by the sodium nitroprusside test, and methyl-α-D-glucoside, m.p. and mixed m.p. 168°C. Anal. Calc. for $C_{10}H_{18}O_6$: C, 51.2; H, 7.7; OMe, 13.3. Found: C, 50.9; H, 7.8; OMe, 13.6.

2,3-Di-O-methyl-4,6-O-isopropylidene-methyl-α-D-glucoside

The *iso*propylidene derivative on methylation with Purdie's reagents gave the corresponding 2,3-di-*O*-methyl ether in quantitative yield. This product sublimed at 100°C. It was readily recrystallized from ether – light petroleum (b.p. 60–110°C.) mixture, m.p. 80°C. Anal. Calc. for $C_{12}H_{22}O_6$: C, 54.9;H, 8.4; OMe, 35.5. Found: C, 55.0; H, 8.8; OMe, 35.0. When this substance was boiled with 50% acetic acid, acetone was produced and evaporation of the solvent left 2,3-di-*O*-methyl-methyl-α-D-glucoside, m.p. 83–84°C. (lit. 83–85°C. (2)).

2,3-Di-O-methanesulphonyl and 2,3-Di-O-toluene-p-sulphonyl 4,6-O-Isopropylidene-methyl-α-D-glucoside

The *iso*propylidene derivative (0.1 gm.) was dissolved in pyridine (10 ml.) and methanesulphonyl chloride (0.5 ml.) was added. The mixture became warm (40°C.) and was then allowed to stand at 20°C. for 20 hr. The solution was poured onto ice and the methanesulphonyl derivative isolated by extraction of the solution with chloroform in the usual manner. The product (0.1 gm.) was recrystallized from aqueous alcohol, m.p. 87°C. Anal. Calc. for $C_{12}H_{22}O_{10}S_2$: C, 36.9; H, 5.6; S, 16.4. Found: C, 36.8; H, 5.6; S, 16.4.

The 2,3-di-*O*-toluene-*p*-sulphonate was prepared in a similar fashion from the *iso*propylidene derivative (0.1 gm.), pyridine (10 ml.), and toluene-*p*-sulphonyl chloride (1.0 gm.). The product was recrystallized from methanol, m.p. 145°C. Anal. Calc. for $C_{24}H_{30}O_{10}S_2$: C, 53.2; H, 5.6; OMe, 11.8. Found: C, 53.3; H, 5.6; OMe, 11.8.

*2,3-Di-O-benzoyl-4,6-O-isopropylidene-methyl-α-*D*-glucoside*

The *iso*propylidene derivative of methyl-α-D-glucoside (2.1 gm.) was dissolved in pyridine (30 ml.) and benzoyl chloride (5 ml.) added. The solution became warm and pyridine hydrochloride began to separate. After 12 hr., water (5 ml.) was added and the mixture poured onto ice. The 2,3-di-*O*-benzoyl derivative was isolated by extraction of the solution with chloroform. The product was recrystallized from acetone methanol. Yield: 2.8 gm., 70%; m.p. 131°C. Anal. Calc. for $C_{24}H_{26}O_8$: C, 65.2; H, 6.0. Found: C, 65.3; H, 6.1.

*Oxidation of 4,6-O-Isopropylidene-methyl-α-*D*-glucoside with Sodium Meta-periodate*

The substance (0.248 gm.) was dissolved in water (5 ml.), a solution of sodium *meta*periodate (5 ml., 0.25 *M*) added, and the change in optical rotation observed. $[\alpha]_D$ +92° (3 min.); +88° (4 min.); +71° (15 min.); +62° (25 min.); +46° (65 min.); +48° (120 min.); +57° (180 min.); +82° (20 hr.) constant value. At the stage of minimum optical rotation approximately one mole of periodate had been consumed per mole of sugar derivative.

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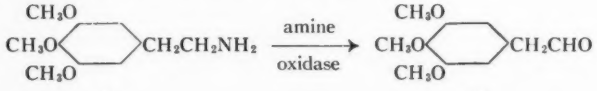
THE SYNTHESIS OF 3,4,5-TRIMETHOXYPHENYLACETALDEHYDE[1]

BY J. G. DUFF AND J. M. PEPPER

As part of a more general program of research concerned with a biochemical study of the hallucinogenic activity of mescaline (I), it was necessary to prepare 3,4,5-trimethoxyphenylacetaldehyde (II). If the primary action of this drug were the deamination by an amine oxidase:



I II

[1]*This note constitutes part of a thesis submitted by J. G. Duff for the degree of Master of Science in Pharmacy, March, 1955.*

then the resulting aldehyde might be considered to show a similar if not even an enhanced activity.

One prior synthesis of this aldehyde has been reported, that by Mauthner (1) who obtained it by the ozonolysis of 3,4,5-trimethoxyallylbenzene. In this work the following alternative synthetic routes were followed:

1. 3,4,5-Trimethoxyallylbenzene was hydroxylated with cold potassium permanganate and the resulting diol was oxidized with either periodic acid or lead tetraacetate to produce the required aldehyde (II).

2. 3,4,5-Trimethoxybenzaldehyde was converted to the homoaldehyde (II) by the application of the Darzens glycidic ester condensation procedure.

From both syntheses the required 3,4,5-trimethoxyphenylacetaldehyde was obtained, after distillation, as a white crystalline solid, m.p. 39–40°C., although previously reported by Mauthner (1) to be an oil.

EXPERIMENTAL[2]

Method 1

3,4,5-Trimethoxyallylbenzene

4-Hydroxy-3,5-dimethoxyallylbenzene, which had been prepared from 2,6-dimethoxyphenol according to the method of Pearl (3), was methylated with dimethyl sulphate in alkali to produce 3,4,5-trimethoxyallylbenzene.

3-(3′,4′,5′-Trimethoxyphenyl)propanediol-1,2

The most satisfactory conditions found for the hydroxylation of 3,4,5-trimethoxyallylbenzene were as follows. 3,4,5-Trimethoxyallylbenzene (20.8 gm.) was dissolved in a mixture of water (100 ml.) and ethanol (200 ml.). Potassium permanganate (5.5 gm.), dissolved in water (1100 ml.), was added in one portion with stirring, the temperature being maintained below 15°C. After three minutes the manganese dioxide was removed by filtration and the aqueous solution concentrated to a volume of 400 ml. This solution was extracted with benzene in a continuous liquid–liquid extractor for an extended length of time. From the resulting benzene extract the crude 3-(3′,4′,5′-trimethoxyphenyl)propanediol-1,2 was obtained by concentration. After recrystallization from benzene – petroleum ether (Skellysolve C), yield 12.2 gm. (52.6%), m.p. 83–84°C. Calc for $C_{12}H_{18}O_5$: C, 59.49; H, 7.49%. Found: C, 59.48; H, 7.46%.

Oxidation of 3-(3′,4′,5′-Trimethoxyphenyl)propanediol-1,2

(*a*) *Using periodic acid.*—3-(3′,4′,5′-Trimethoxyphenyl)propanediol-1,2 (6.4 gm.) was dissolved in water (300 ml.). Paraperiodic acid (3.7 gm.) was dissolved in water (200 ml.) and this solution added dropwise to the former. After 30 min., lead nitrate (10%, 100 ml.) was added and the precipitate removed by filtration. The filtrate was extracted with ether (5×50 ml.) and then with benzene (50 ml.). The combined extracts were dried over anhydrous sodium sulphate and the solvents removed. Distillation (bath temperature, 160–190°C. at 0.05 mm.) of the residue yielded 3,4,5-trimethoxyphenylacetaldehyde (1.85 gm., 31.1%) as a viscous pale yellow oil which readily

[2]*All melting points are uncorrected.*

crystallized on seeding, m.p. 39–40°C.; semicarbazone, m.p. 186–187°C., reported m.p. 188°C. (1).

(*b*) *Using lead tetraacetate.*—3-(3′,4′,5′-trimethoxyphenyl)propanediol-1,2 (5 gm.) was dissolved in dry benzene (55 ml.) and placed in a three-necked flask provided with a magnetic stirrer and condenser. Under reflux, lead tetraacetate (9.3 gm.) was added in small portions. After completion of the addition, the mixture was refluxed for 10 min. After cooling, the mixture was filtered, the benzene washed with water, dried, and removed by distillation. The residue was distilled (bath temperature, 160–190°C. at 0.05 mm.) to yield 3,4,5-trimethoxyphenylacetaldehyde (2.2 gm., 50.9%) as a viscous pale yellow oil which crystallized on seeding, m.p. 39–40°C.; semicarbazone, m.p. 186–188°C.

Method 2

Darzens Glycidic Ester Condensation (*2*)

From 3,4,5-trimethoxybenzaldehyde (14.8 gm.), prepared in a 75.6% yield by the methylation of syringaldehyde, and ethyl chloroacetate (9.0 gm.) with sodium ethoxide as a catalyst, there was obtained the white intermediate glycidic ester which, after recrystallization from water–ethanol, weighed 4.0 gm. This solid was added to a solution of hydrochloric acid (1.3 ml.) and water (6.8 ml.) in a flask fitted with a reflux condenser, and when it was gently warmed, gas was evolved and an oily layer separated. After one and one-half hours, the reaction mixture was cooled and extracted with benzene. This extract was washed with water (20 ml.), dried over anhydrous sodium sulphate, and concentrated to remove the solvent. Distillation (bath temperature, 160–190°C. at 0.05 mm.) of the residue yielded 3,4,5-trimethoxyphenylacetaldehyde (0.6 gm., 3.7%) as a clear viscous oil which readily crystallized, m.p. 39–40°C. Calc. for $C_{11}H_{14}O_4$: C, 62.84; H, 6.71%. Found: C, 62.07; H, 6.56%. The semicarbazone melted at 187–188°C.

A mixed melting point between samples of the semicarbazones prepared from the 3,4,5-trimethoxyphenylacetaldehydes made by each method showed no depression, being at 187–188°C.

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